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Contributions from the Sheffield Laboratory of Yale College.

XVIII.—THE SEPARATION OF ZINC AND NICKEL.

BY THOMAS B. OSBORNE.

Having experienced considerable difficulty in separating zinc and nickel according to the directions given in Fresenius' Quantitative Analysis, I determined to find out the exact conditions under which the best separation could be effected. I prepared several solutions of zinc and nickel sulphates, containing about .4 gram zinc and .3 gram nickel, in 300 cc. of water slightly acidified with sulphuric acid. To these I added carbonate of soda until a slight but permanent precipitate was formed, which remained after stirring and standing, and then added four drops of hydrochloric acid (sp. gr. 1.1) to the first, six to the second, eight to the third, and so on, adding eighteen to the last. Into these liquids I led sulphuretted hydrogen gas for an hour and a half, and during the precipitation added a solution containing enough sodium acetate to react with half the acid set free by the precipitation of the zinc. On standing, all the zinc and nickel precipitated from the solution containing four drops of acid, and pure white zinc sulphide was only obtained in those solutions containing ten or more drops, and the filtrate from these contained no zinc.

I then sought to determine how much hydrochloric acid the solution might contain without keeping the zinc in solution. On increasing the amount to 2 cc. hydrochloric acid (sp. gr. 1.1) in

300 cc. of water, I found that a very little zinc remained in solution after passing the sulphuretted hydrogen gas two hours. The rule I established from the above experiments was to add carbonate of soda solution until a slight but permanent precipitate formed, then 1 cc. hydrochloric acid (sp. gr. 1.1), and gradually during the precipitation of the zinc 50 cc. of a solution containing enough sodium acetate to react as near as may be with one-half the acid set free. Sulphuretted hydrogen gas was passed an hour and a half. In this way a certain separation can be secured, and the zinc will be snow white.

Brunner's directions, if accurately followed, will give a good separation, but they are rather indefinite on the vital point, namely, the amount of hydrochloric acid to be added. He says a *few* drops should be added, which if taken to mean ten or twelve would give good results if too much zinc were not present; for if a large amount of zinc were in solution, its precipitation would set free so much acid that "the few drops of a very dilute solution of sodium acetate" which he adds, would not suffice to effect its complete precipitation. His theory of the action of sodium acetate made the amount of this quite independent of the amount of zinc, as he considered it as forming zinc acetate, which was precipitated by hydrogen sulphide, and the acetic acid thus set free reacted with more zinc until all was precipitated. The office of sodium acetate is of course to form acetic acid and sodium chloride or sulphate as the case may be, reacting with the acid set free by the precipitation of the zinc. Fresenius is more explicit in regard to the amount of hydrochloric acid which should be added, but he recommends only two or three drops, which in most cases is too little. The basic zinc carbonate is quite soluble in a solution of carbonic acid, and consequently a *permanent* precipitate is often not obtained until there is an appreciable excess of sodium carbonate, which will sometimes require as much as three or four drops of hydrochloric acid to neutralise it. Hence to be certain of a good separation, at least 1 cc. hydrochloric acid (sp. gr. 1.1) should be added; and that the amount of free hydrochloric acid shall remain as nearly constant as possible, enough sodium acetate should be added to react with about one-half the acid set free by precipitation. It is hardly safe to add more, lest some nickel may be thrown down. When ammonium salts will not interfere with the subsequent determination of the nickel, ammonia is much more convenient to use than sodium carbonate. This should be added until a precipitate is

formed, then hydrochloric acid until this precipitate is just dissolved, and two or three drops added in excess, the hydrogen sulphide passed and the sodium acetate solution added as before. If ammonia gives no precipitate, owing to the presence of too much ammonium salts, a neutral reaction with test paper may be obtained, and an excess of four or five drops of hydrochloric acid added. Ammonia is much more easily employed than carbonate of soda, and when the nickel is determined by precipitation with ammonium sulphide, and then as metal with the battery, the ammonium salts are beneficial rather than otherwise.

XIX.—THE SEPARATION OF ZINC IN ORES, &c.

By Thomas B. Osborne.

Although Brunner[1] states that zinc cannot be separated from iron by his method for the separation of zinc from nickel, I have found that, under certain conditions at least, it can be done, and that, too, very perfectly. I tested for iron several precipitates of zinc sulphide precipitated from solutions containing iron, and obtained only the very faintest tinge of red with ammonium sulphocyanate. The filtrates from these sulphides I examined with care for zinc and found none; I then tried this process for the separation of zinc from its ores and obtained very accurate results.

Silica was first removed from the ores, and then any iron that was present in the ferric state reduced by warming with sulphurous acid, so that there might be as little hydrochloric acid as possible liberated from the reduction of iron by the subsequent passage of hydrogen sulphide.

The solution was cooled and ammonia added till a slight permanent precipitate formed. This was dissolved in hydrochloric acid (sp. gr. 1.1), and four or five drops added in excess. The volume was then brought to 300 cc. and hydrogen sulphide passed one hour and a half. Fifty cubic centimeters of a solution containing a sufficient quantity of sodium acetate to react as nearly as could be estimated with one-half the acid set free by the precipitation of the zinc, were added gradually. The zinc sulphide was filtered, washed, dissolved in hydrochloric acid, and precipitated with sodium carbonate and weighed as oxide.

[1] Dingler's Polyt. Jour. **150**, 369.

When a large amount of zinc is precipitated in this way, sodium acetate should be added in such quantity that there will be only about .2 gram of hydrochloric acid gas left free in 300 cc. of the solution after precipitating all the zinc. As it is not always possible to know approximately how much zinc is present, the proper amount of sodium acetate to add cannot be determined with accuracy. But some latitude is permissible here, as the zinc can be precipitated in a solution containing even .4 gram hydrochloric acid gas in 350 cc. of water, as shown by Eliot and Storer's[1] experiments and confirmed by my own. It should be borne in mind, however, that the more acid there is present the greater is the liability of an incomplete precipitation.

Several analyses by this process gave results agreeing closely with analyses made by Dr. A. B. Howe of this laboratory, who removed iron by precipitating it twice as basic ferric acetate, and separated zinc from manganese as sulphide in an acetic acid solution, determining zinc finally as oxide. The results of these analyses were as follows:

By direct precipitation as sulphide in hydrochloric acid solution,

	Ores.			Slag.
ZnO	27.73	20.11	27.78	2.08

By separating iron as basic acetate, &c.

ZnO	27.87	20.10	27.23	2.04

Zinc was determined by this method in three solutions made up as follows:

$Ca(OH)_2$	.3	gram.	.2	gram.
$MnCl_2$	.2	"	.2	"
$Al_2(SO_4)_3$	.2	"		
$MgSO_4$	.2	"	.2	"
$FeSO_4$	.5	"	.5	" 4.6
Zinc	.3392	"	.3040	" .0202
Zinc found,	.3410	"	.3035	" .0210

I found that sulphuric acid (1 volume strong acid to three of water) can be used as well as hydrochloric acid (sp. gr. 1.1) to keep the iron and other members of the first four groups (according to Fresenius) from precipitating with the zinc. It should be used in the same amount by volume. By this process zinc can be determined in an ore in five or six hours, as the zinc sulphide need not settle before filtering if the amount of free hydrochloric acid is small.

[1] Mem. Am. Acad. Arts and Sciences **8**, 95.

THE QUANTITATIVE ESTIMATION OF CARBON IN ORDINARY PHOSPHORUS.

By Ira Remsen and E. H. Keiser.

In our last communication[1] in which we furnished proof of the presence of carbon in ordinary phosphorus, we referred to some attempts made by us to estimate the carbon quantitatively. These attempts were not satisfactory. We have since continued the work, and have succeeded in devising a method which gives fair results. In brief it consists in oxidising a known weight of phosphorus by means of pure concentrated nitric acid, removing the oxides of nitrogen from the escaping gases, collecting and weighing the carbon dioxide. The apparatus used is, first, a glass-stoppered retort of about 500 cc. capacity. This is placed with the neck inclined upward at an angle of about 30°, and connected by means of glass tubing and gypsum joints with one of the wash bottles described in our last paper. This in turn is connected in a similar way with a combustion tube placed on a furnace. At the other end of the combustion tube connection is made with two wash bottles like the one above referred to. In the retort are placed two to three hundred cubic centimetres of pure nitric acid of specific gravity 1.2, and a weighed amount of ordinary phosphorus. In the first wash bottle there is pure water. The combustion tube is filled to about half its length with granulated metallic copper, and a short layer of granulated copper oxide. In the first of the last two wash bottles is pure water, and at the proper time a clear solution of baryta water containing some caustic soda is brought into the second. Finally this last wash bottle is protected from the air by a tube filled with caustic soda. After the apparatus is arranged as thus indicated, a slow current of air free from carbon dioxide is drawn slowly through it until all the original air is displaced. Now the retort is closed by means of a glass stopper, the baryta water and caustic soda are introduced into the last wash bottle, and the heating of the retort and the combustion tube is begun. A very small flame is used, and a regular, slow evolution of gas is secured. A portion of the tetroxide of nitrogen is, of course, decomposed by the water in the first wash bottle; what

[1] This Journal 5, 424.

remains passes on, together with the other oxides, to the heated copper which decomposes them. The copper oxide serves to oxidise any carbon monoxide which may possibly have escaped complete oxidation.

It will thus be seen that the gases do not come in contact with organic matter at any point. A blank experiment showed that, when purified air was passed through the heated nitric acid, and in other respects treated as in the experiments with phosphorus, no precipitate was formed in the baryta water. When the phosphorus was introduced into the nitric acid, however, a precipitate was clearly perceptible in about half an hour from the beginning of the heating. It increased and became very decided in the course of two or three hours, the time usually occupied by the experiment. When the oxidation is finished, air free from carbon dioxide is again slowly drawn through the apparatus until the gases have been displaced. The bottle containing the barium carbonate is then removed, closely stoppered, and the precipitate allowed to settle. It is then rapidly filtered off with the aid of a filter pump, washed, and dissolved in dilute hydrochloric acid. The effervescence caused by the acid leaves no room for doubt as to the character of the precipitate. The barium is now estimated as sulphate. The filtrate from the sulphate was carefully examined for compounds of phosphorus, but not a trace was found. In two cases the carbon dioxide was collected directly in caustic potash contained in bulbs which were weighed before and after the experiment. In three analyses a considerable quantity (from sixty to eighty grams) of phosphorus was placed in the retort, and the oxidation continued for about three hours. The unoxidised phosphorus was then weighed, the difference between this weight and the original weight of the phosphorus showing the amount oxidised. Closely agreeing results can hardly be expected, yet it will be seen that the agreement is fairly good, if we leave out the second analysis, which for some unknown reason gives a considerably larger percentage than the others. The results of six analyses are here given:

I. 6.2272 grams phosphorus gave 0.0300 gram $BaSO_4$ = 0.0057 gram CO_2 = 0.0016 gram C = *0.026 per cent. carbon.*

II. 7.9545 grams phosphorus gave 0.0324 gram CO_2 = 0.0088 gram C = *0.111 per cent. carbon.*

III. 8.8041 grams phosphorus gave 0.0134 gram CO_2 = 0.00365 gram C = *0.042 per cent. carbon.*

IV. 9.0650 grams phosphorus gave 0.0540 gram $BaSO_4$ = 0.0101 gram CO_2 = 0.00278 gram C = *0.031 per cent. carbon.*

V. 16.4633 grams phosphorus gave 0.1303 gram $BaSO_4$ = 0.0246 gram CO_2 = 0.0067 gram C = *0.041 per cent. carbon.*

VI. 11 grams phosphorus gave 0.0929 gram $BaSO_4$ = 0.0175 gram CO_2 = 0.00478 gram C = *0.043 per cent. carbon.*

The figures speak for themselves. While the absolute quantity of carbon present in the phosphorus is small, it is quite sufficient to account for the results obtained by us in passing air alone over phosphorus, and we consider that the question regarding the action of moist phosphorus on carbon monoxide and air as definitely settled. There is no proof whatever in favor of the view that the carbon monoxide is oxidised. We say this deliberately after having read carefully the last communication of Professor Baumann,[1] in which he states that when air alone is passed over phosphorus it produces no precipitate in baryta water. That is the real point at issue. Upon that we differ diametrically. We invite others to repeat our experiments, and sincerely hope that some may do so.

Contributions from the Chemical Laboratory of Harvard College.

XL.—ON β-BROMTETRACHLORPROPIONIC ACID.

By Charles F. Mabery.

With the hope of establishing the structure of certain bromdichloracrylic acids which I have at present under examination, I endeavored to prepare an acid of the same empirical composition by the addition of a molecule of chlorine to brompropiolic acid.[2]

In studying the relations of these substances toward each other under different conditions, it was found that the action of chlorine upon the melted acid was so violent that frequently it resulted in an explosion. Even at ordinary temperatures a gaseous product

[1] Berichte der deutschen chemischen Gesellschaft **17**, 283.

[2] In a former paper (Mabery and Robinson, this Journal **5**, 255, and Proceedings Amer. Academy **18**, 45), it was stated that a bromdichloracrylic acid could be prepared by passing chlorine through a chloroform solution of brompropiolic acid cooled to 0°. This statement was evidently made upon insufficient evidence, since all subsequent attempts to obtain the same result have proved unsuccessful.

was freely evolved, with a disagreeable odor resembling that of phosgene.

As previous experiments had shown, in a chloroform solution of the acid the action of chlorine could easily be controlled; in fact, for some time it could not be determined whether the addition had begun, since evaporation of the chloroform left only a pasty mass which refused to crystallise. Finally, after continuing the action for several hours, a crust began to form above the solution, and soon the greater part of a crystalline addition product was deposited.

This substance proved to be sparingly soluble in cold carbonic disulphide and chloroform, more soluble in hot, and after purification it melted with decomposition at 225°. The percentage composition calculated from the results of analysis corresponds to that of bromtetrachlorpropionic acid.

I. 0.2000 gram of the substance gave 0.5235 gram AgBr + AgCl.

II. 0.5874 gram of the substance gave 0.2732 gram CO_2 and 0.0268 gram H_2O.

III. 0.5385 gram of the substance gave 0.2330 gram CO_2.[1]

	Calculated for $C_3HCl_4BrO_2$.	Found. I.	II.	III.
C	12.37		12.67	11.82
H	.34		.51	
4Cl + Br	76.30	76.26		

The salts of this acid are extremely unstable. It dissolves readily in sodic or potassic carbonate, or in ammonic hydrate, and is precipitated by hydrochloric acid; yet the corresponding salts could not be prepared sufficiently pure for analysis. When treated with baric carbonate, the acid dissolves with the formation at first of a clear solution; but soon the latter becomes turbid from the separation of an oil, which continues until the decomposition of the salt is complete. Although this oil was not submitted to analysis, it is probably tetrachlorethylene. The silver salt which is formed when argentic nitrate is brought in contact with the acid, soon changes color, even in the dark, and all attempts to prepare it in a form suitable for analysis were unsuccessful.

Unless a molecular rearrangement takes place during the addi-

[1] By accident the water in this combustion was lost.

tion of chlorine, which does not seem at all probable, the structure of this acid must be represented by the formula:

$$\begin{array}{l} CBrCl_2 \\ | \\ CCl_2 \\ | \\ COOH. \end{array}$$

Many variations of the method of preparation above described have been tried in order, if possible, to limit the addition of chlorine to the formation of a bromdichloracrylic acid. The appearance of the product and its behavior toward solvents at different stages of the chlorination would seem to indicate that each molecule of brompropiolic acid absorbed two molecules of chlorine, thereby forming a mixture of bromtetrachlorpropionic acid and unaltered brompropiolic. This would, of course, preclude the possibility of obtaining by the addition of chlorine the corresponding substituted acrylic acid.

XLI.—ON α- AND β-CHLORDIBROMACRYLIC ACIDS.[1]

By Charles F. Mabery and Rachel Lloyd.

α-CHLORDIBROMACRYLIC ACID.

In a former paper by F. C. Robinson and one of us,[2] a brief account was given of certain experiments in which we had tried to obtain an addition product of brompropiolic acid with chlorine monobromide. Although the results then obtained were rather unsatisfactory, it seemed possible nevertheless to prepare the addition product in a state of purity, and this became especially desirable when it was found that an acid of the same empirical composition could be formed from chlortribrompropionic acid.

In resuming the study of this reaction, it was evidently necessary to secure at the outset a combination of the halogens containing no free bromine, inasmuch as previous results had shown that a small percentage even of tribromacrylic acid could not be removed from the product by crystallisation. On the other hand, an excess of chlorine was not objectionable, since it had been found that this substance in the free state united much less readily with brompro-

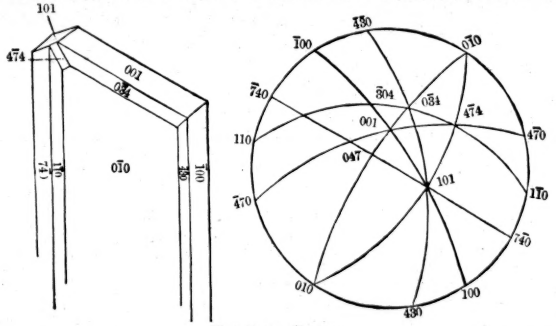
[1] The results described in papers XLI, XLII, and XLIII were obtained under my direction in the summer course of instruction in chemistry for 1883.—C. F. M.

[2] This Journal **5**, 254; and Proceedings Amer. Acad. **18**, 41.

piolic acid than when combined with bromine. The chlorine monobromide used to form this addition product was therefore made by saturating bromine at 0° with chlorine; and to insure complete saturation the resulting product was dissolved in chloroform and this solution saturated at 0°. Brompropiolic acid was then added gradually, taking care to keep the solution cold and the chlorine monobromide in excess. Chemical action immediately ensued, and the formation of the addition product was complete after standing half an hour. Evaporation of the chloroform left a solid residue, which was easily purified by crystallisation from hot water.

This acid is sparingly soluble in cold, very soluble in hot water, more soluble in hot than in cold carbonic disulphide, and very soluble in chloroform. Its melting point is 104°. By slow evaporation it separates from a solution in carbonic disulphide in triclinic prisms. These crystals have been submitted to careful study by Mr. Oliver W. Huntington,[1] to whom we are indebted for the following results:

CRYSTALLINE FORM OF *a*-CHLORDIBROMACRYLIC ACID.



Triclinic System.

Forms [100], [010], [001], [101], [1$\bar{1}$0], [430], [0$\bar{3}$4], [$\bar{3}$04], [7$\bar{4}$0], [$\bar{4}$70], [$\bar{4}$74], [047]?

From the fundamental angles the following values were calculated:

X on Y 104° 43′, Y on Z 71° 6, X on Z 71° 10;

$a : b : c = 0.7981 : 1 : 0.7207.$

[1] Proceedings Amer. Acad. **18**, 282.

Angles between Normals.

	Observed.		Calculated.
010 on 100	66° 23′	}	
100 " 001	116° 17′		
010 " 001	116° 20′	} Fundamental angles.	
100 " 101	63° 50′		
100 " 1$\bar{1}$0	47° 5′	}	
100 " 430			23° 52′
100 " 7$\bar{4}$0	27°		27° 5′
010 " $\bar{4}$70	42° 26′		42° 36′
001 " 0$\bar{3}$4	21°		21°

In the paper above referred to Mr. Huntington makes the following remarks concerning the planes [430], [0$\bar{3}$4], [$\bar{3}$04], [7$\bar{4}$0], [$\bar{4}$70], [4$\bar{7}$4], [047]?: "These symbols were for the most part deduced from the zone intersections, and the indices could only in a few cases be verified by angular measurements. The faces of the vertical prism especially were very irregular, in consequence of the alternations caused by parallel grouping, so common with artificial crystals; and although the relative position of the fundamental planes could be accurately fixed, the symbols of the intermediate planes must be regarded as doubtful; these planes were seldom seen, and only in the vertical zone. The symbols given on the projection were obtained by finding the intersection with the vertical zone of other zones never well defined on the same crystal, and it can only be claimed that the approximate angular measurements on the vertical zone were compatible with the indices given above."

The composition of the purified acid was shown by analysis:

I. 0.2254 gram of the substance gave 0.4435 gram AgCl + AgBr.

II. 0.2046 gram of the substance gave 0.3980 gram AgCl + AgBr.

III. 0.8187 gram of the substance gave 0.3920 gram CO_2 and 0.0273 gram H_2O.

	Calculated for $C_2HCl_2BrO_2$.	Found. I.	II.	III.
2Cl + Br	73.91	74.03	73.19	
C	13.56			13.05
H	.38			.37

In determining the solubility of this acid in cold water according

to the method of V. Meyer, a saturated solution was neutralised with baric carbonate, and the barium determined in the filtered solution by precipitation with sulphuric acid.

I. 11.0890 grams of a solution saturated at 20° gave 0.2344 gram $BaSO_4$.

II. 1.6299 grams of a solution saturated at 20° gave 0.0379 gram $BaSO_4$.

From these results the following percentages were calculated:

I.	II.
5.18	5.68

The barium, calcium, potassium, and silver salts of this acid were prepared and analysed.

Baric α-Chlordibromacrylate, $Ba(C_3ClBr_2O_2)_2.3H_2O$. — On saturating an aqueous solution of the acid with baric carbonate a neutral solution was obtained, from which, by evaporation, the barium salt separated in elongated flat prisms with oblique terminations. This salt is much less soluble in cold than in hot water. The crystals which separated from a hot solution were first dried to a constant weight in the air, then heated to 80°.

0.9545 gram of the air-dried salt lost 0.0712 gram H_2O at 80°.

0.8790 gram of the anhydrous salt gave 0.3083 gram $BaSO_4$.

	Calculated for $Ba(C_3ClBr_2O_2)_2.3H_2O$.	Found.
H_2O	7.46	7.52
	Calculated for $Ba(C_3ClBr_2O_2)_2$.	
Ba	20.63	20.62

The solubility of the barium salt in cold water was also determined.

I. 1.4307 grams of a solution saturated at 20° gave 0.1190 gram $BaSO_4$.

II. 2.5352 grams of a solution saturated at 20° gave 0.2142 gram $BaSO_4$.

The results correspond to the following percentages:

I.	II.
20.46	20.70

Calcic α-Chlordibromacrylate, $Ca(C_3ClBr_2O_2)_2.2\frac{1}{2}H_2O$.—The calcium salt was prepared by neutralising an aqueous solution of the acid with calcic carbonate. From the concentrated solution the salt separated in irregular branching needles, which lost two

and one half molecules of crystal water at 80°, after drying to constant weight in the air.

I. 1.2644 grams of the air-dried salt lost 0.1006 gram H_2O at 80°.

II. 0.9273 gram of the air-dried salt lost 0.0714 gram H_2O at 80°.

	Calculated for $Ca(C_3ClBr_2O_3)_2\ 2\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	7.80	7.95	7.70

I. 0.8166 gram of the anhydrous salt gave on ignition with H_2SO_4 0.2016 gram $CaSO_4$.

II. 0.8328 gram of the anhydrous salt gave 0.1835 gram $CaSO_4$.

	Calculated for $Ca(C_3ClBr_2O_3)_2$.	Found. I.	II.
Ca	7.05	7.26	6.47

Potassic α-Chlordibromacrylate, $KC_3ClBr_2O_2$?—A solution of the aid was carefully neutralised with potassic carbonate, evaporated to a small volume on the water bath, and finally to dryness over sulphuric acid. It formed a deliquescent amorphous crust, in which the potassium was determined after drying at 80°.

1.0508 gram of the salt dried at 80° gave 0.3124 gram K_2SO_4.

	Calculated for $KC_3ClBr_2O_2$.	Found.
K	12.92	13.36

Argentic α-Chlordibromacrylate, $AgC_3ClBr_2O_2$. — The silver salt was prepared by the addition of argentic nitrate to an aqueous solution of the barium salt. It separated as a curdy precipitate, which could be recrystallised from hot water without perceptible decomposition. It crystallises in rhombic plates, and is not affected by ordinary daylight.

0.4715 gram of the salt gave 0.1799 gram AgCl.

	Calculated for $AgC_3ClBr_2O_2$.	Found.
Ag	29.07	28.72

β-CHLORDIBROMACRYLIC ACID.

The readiness with which chlortribrompropionic acid is decomposed by alkaline hydrates has already been described,[1] and chlordibromethylen was identified as one of the products when the decomposition was effected with the aid of heat in a strongly alkaline solution.

[1] This Journal **5**, 255; and Proceedings Amer. Acad. **18**, 45.

A more careful study of the conditions has shown that a halogen atom may be eliminated without severing the connection of the carbon atoms. If the solution is kept cold, and a calculated amount of the alkaline hydrate — by preference baric hydrate — is added slowly, it will retain its acid reaction until the change represented by the following equation is nearly complete:

$$2C_3ClBr_3O_2H_2 + 2BaO_2H_2 = Ba(C_3ClBr_3O_2)_2 + BaBr_2 + 4H_2O.$$

The solution must then be made slightly alkaline, and kept so for twenty-four hours. On acidifying with hydrochloric acid, the resulting chlordibromacrylic acid is partially precipitated as an oil, and the remainder may be extracted from the solution with ether.

The acid is purified by crystallisation from hot water, in which it is far more soluble than in cold. It is very soluble in ether and alcohol, less soluble in carbonic disulphide and chloroform. By slow evaporation from a solution in carbonic disulphide it crystallises in oblique prisms, which melt at 99°.

Several attempts were made by Mr. Huntington to determine the crystalline form of this acid in order to compare it with that of α-chlordibromacrylic acid. But unfortunately all the crystals we were able to obtain for that purpose gave very imperfect reflections, and Mr. Huntington was able to say only that in their general habit they resembled closely those he had already measured of the α-acid. A few planes gave fairly good reflections, and the angles thus measured were nearly the same as those of the α-acid.

	α-Chlordibromacrylic Acid.	β-Chlordibromacrylic Acid.	Calculated.
010 on 100	66° 23′	67°	
010 " $\bar{4}70$	42° 26′	44° 25′	
010 " $\bar{7}40$		42° 26′	42° 36′

The composition of the purified acid was established by analysis.

I. 0.2472 gram of the substance gave 0.4869 gram AgCl + AgBr.

II. 0.2060 gram of the substance gave 0.4016 gram AgCl + AgBr.

III. 0.7566 gram of the substance gave 0.3690 gram CO_2 and 0.0325 gram H_2O.

IV. 0.4714 gram of the substance gave 0.2319 gram CO_2 and 0.0227 gram H_2O.

	Calculated for $C_3HClBr_2O_2$.	Found. I.	II.	III.	IV.
Cl + 2Br	73.91	74.09	73.33		
C	13.61			13.30	13.42
H	.38			.48	.54

The solubility of the acid was determined by the method of V. Meyer. After neutralisation with baric carbonate the barium was precipitated from the filtered solution with sulphuric acid.

I. 7.1822 grams of a solution saturated at 20° gave 0.0789 gram $BaSO_4$.

II. 5.3623 grams of a solution saturated at 20° gave 0.0548 gram $BaSO_4$.

From these results the following percentages were calculated:

I.	II.
2.69	2.50

A study of the salts of this acid developed important differences between them and the corresponding salts of α-chlordibromacrylic acid.

Baric β-Chlordibromacrylate, $Ba(C_3ClBr_2O_2)_2.3H_2O$.—A solution of the acid was heated with an excess of baric carbonate, filtered, and concentrated by evaporation. On cooling, the barium salt crystallised in oblique slender prisms, which were somewhat more soluble in cold water than the barium salt of the α-acid. After drying to a constant weight in the air the salt contained three molecules of crystal water, which were slowly given up over sulphuric acid, but more rapidly at 80°.

I. 0.7765 gram of the air-dried salt lost 0.0565 gram H_2O at 80°.

II. 1.0502 grams of the air-dried salt lost 0.0782 gram H_2O at 80°.

III. 0.7185 gram of the anhydrous salt gave 0.2462 gram $BaSO_4$.

IV. 0.5975 gram of the anhydrous salt gave 0.2051 gram $BaSO_4$.

	Calculated for $Ba(C_3ClBr_2O_2)_2.3H_2O$.	Found. I.	II.
H_2O	7.52	7.27	7.45
	Calculated for $Ba(C_3ClBr_2O_2)_2$.	III.	IV.
Ba	20.63	20.15	20.18

In determining the solubility of the barium salt in cold water the following results were obtained:

I. 1.5511 grams of a solution saturated at 20° gave 0.1413 gram $BaSO_4$.

II. 1.8345 grams of a solution saturated at 20° gave 0.1676 gram $BaSO_4$.

The solubility of the salt in water at 20° is therefore shown by the following percentages:

I.	II.
25.90	26.04

Calcic β-Chlordibromacrylate, $Ca(C_3ClBr_2O_2)_2.4H_2O$.—On concentrating a solution of the calcium salt prepared by neutralising a solution of the acid with calcic carbonate, the salt separated in clusters of branching needles, which were less soluble in water than the calcium salt of the α-acid.

I. 1.2644 grams of the air-dried salt lost 0.1345 gram H_2O at 80°.

II. 0.9273 gram of the air-dried salt lost 0.1038 gram H_2O at 80°.

III. 1.2124 grams of the air-dried salt lost 0.1328 gram H_2O at 80°.

IV. 0.8820 gram of the anhydrous salt gave 0.1887 gram $CaSO_4$.

	Calculated for $Ca(C_3ClBr_2O_2)_2.4H_2O$.	Found. I.	II.	III.
H_2O	11.27	10.64	11.19	10.91
	Calculated for $Ca(C_3ClBr_2O_2)_2$.			
Ca	7.05		6.75	

Potassic β-Chlordibromacrylate, $KC_3ClBr_2O_2$?—When a solution of the acid was neutralised with potassic carbonate, concentrated on the water bath, and evaporated to dryness over sulphuric acid, the potassium salt was left in the form of a very deliquescent amorphous mass. For analysis the salt was finally dried at 80°.

1.0509 grams of the salt gave 0.4397 gram K_2SO_4.

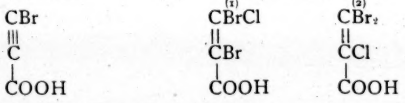
	Calculated for $KC_3ClBr_2O_2$.	Found.
K	12.92	12.42

All attempts to prepare a silver salt of this acid were unsuccessful. On the addition of argentic nitrate to a solution of the acid or any of its salts, the solution immediately became turbid from the separation of argentic bromide. This decomposition was not prevented to any appreciable extent by the exclusion of light.

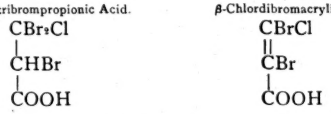
CONSTITUTION OF α- AND β-CHLORDIBROMACRYLIC ACIDS.

The essential points of difference in the physical properties of these acids, which appear in their general behavior and solubility in water, as well as in their melting points, would seem to point to a difference in structure. In the degree of hydration, solubility in water and comparative stability, their salts exhibit peculiarities as marked as those of the acids themselves. Although the silver salt of the α-acid can be prepared without difficulty, the corresponding salt of the β-acid cannot be formed even with the greatest care.

While the product obtained by the action of chlorine monobromide upon brompropiolic acid may have one of two forms,—



the acid resulting from the abstraction of the elements of hydrobromic acid from chlortribrompropionic acid can evidently have but one:



Since the formula of β-chlordibromacrylic acid is identical with (1), the structure of the α-acid is probably represented by (2); or during the addition of chlorine monobromide to brompropiolic acid, the weaker halogen unites with the terminal carbon atom.

XLII.—ON β-DIBROMDICHLORPROPIONIC AND β-BROMDICHLORACRYLIC ACIDS.

BY CHARLES F. MABERY AND H. H. NICHOLSON.

β-DIBROMDICHLORPROPIONIC ACID.

In a brief examination of the action of chlorine on β-dibromacrylic acid, it was found by F. C. Robinson and one of us,[1] that, although

[1] This Journal **5**, 254; and Proceedings Amer. Acad. **18**, 44.

the acid was not affected at ordinary temperatures, an addition-product could readily be obtained by raising the temperature. Further study of this reaction shows that the most desirable results are obtained as regards time, as well as the quality and quantity of the product, if the temperature is kept near 100°. In one experiment, after continuing the action for eight hours, 5.9 grams β-dibromacrylic acid gave 7.9 grams of the crude β-dibromdichlorpropionic acid, which melted without purification above 90°, or ninety-six per cent. of the amount of pure acid theoretically required.

The crude acid was easily purified by two or three crystallisations from a hot solution in carbonic disulphide, which deposited the greater part of the acid when cooled to 0°. It is but sparingly soluble in water, more soluble in hot than in cold chloroform, and very soluble in ether and alcohol. It crystallises in oblique prisms, which melt at 100° and sublime slowly at higher temperatures. The composition of this acid was determined by the following analyses:

I. 0.2142 gram of the substance gave 0.4712 gram AgCl + AgBr.

II. 0.8223 gram of the substance gave 0.3485 gram CO_2 and 0.0510 gram H_2O.

	Calculated for $C_3H_2Cl_2Br_2O_2$.	Found. I.	II.
Cl + Br	76.74	76.67	
C	11.96		11.55
H	.66		.69

The salts of this acid are comparatively unstable. We were unable to prepare a silver salt in a form suitable for analysis, since argentic bromide began to separate as soon as argentic nitrate came in contact with the acid. Although there was no perceptible decomposition of the acid when it was treated in the cold with baric carbonate, several different preparations of the salt proved on analysis to contain a quantity of barium nearly three per cent. in excess of the calculated value. In the preparation of the calcium and potassium salts we found less difficulty.

Calcic β-Dibromdichlorpropionate, $Ca(C_3Cl_2Br_2O_2H).1\frac{1}{2}H_2O$.—On treating the acid with calcic carbonate and calcic hydrate in the cold, filtering, and concentrating by spontaneous evaporation at the ordinary temperature, the calcium salt separated in clumps of needles. After drying to a constant weight in the air the salt lost one and a half molecules of crystal water at 80°.

I. 0.7775 gram of the air-dried salt lost 0.0307 gram H_2O at 80°.

II. 0.9392 gram of the anhydrous salt lost 0.0403 gram H_2O at 80°.

III. 0.8626 gram of the anhydrous salt gave 0.1796 gram $CaSO_4$.

	Calculated for $Ca(C_3HCl_2Br_2O_2)_2.1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	4.05	3.95	4.29
	Calculated for $Ca(C_3HCl_2Br_2O_2)_2$.		
Ca	6.25	6.13	

Potassic β-*Dibromdichlorpropionate*, $K(C_3HCl_2Br_2O_2).2H_2O$.—The potassium salt was made by neutralising the acid with an aqueous solution of potassic carbonate and allowing it to evaporate without the application of heat. The air-dried salt contained two molecules of crystal water, which it lost over sulphuric acid.

I. 0.8735 gram of the air-dried salt lost 0.0809 gram H_2O over H_2SO_4.

II. 0.7933 gram of the anhydrous salt gave 0.2171 gram K_2SO_4.

	Calculated for $KC_3HCl_2Br_2O_2.2H_2O$.	Found.
H_2O	9.66	9.26
	Calculated for $KC_3HCl_2Br_2O_2$.	
K	11.53	12.28

β-BROMDICHLORACRYLIC ACID.

β-dibromdichlorpropionic acid is readily decomposed by alkaline hydrates, and when the reaction is allowed to progress in the cold, the elements of hydrobromic acid are eliminated with the formation of the corresponding substituted acrylic acid. The best results were obtained by treating the acid with an aqueous solution of baric hydrate in slight excess over the calculated amount, and keeping the solution slightly alkaline for twenty-four hours. Upon acidifying this solution with hydrochloric acid, dichlorbromacrylic acid was partially precipitated as an oil, which solidified when cooled to 0°. Since the acid is quite soluble in water, the solution was extracted with ether, and the total product was purified by several crystallisations from hot water.

This acid is very soluble in hot, rather sparingly soluble in cold water, and very soluble in carbonic disulphide, chloroform, ether, and alcohol. It crystallises from water in large pearly scales, which melt at 75°–78°. Its composition was determined by analysis.

I. 0.2374 gram of the substance gave 0.5059 gram AgCl + AgBr.

II. 0.2034 gram of the substance gave 0.4377 gram AgCl + AgBr.

III. 0.7255 gram of the substance gave 0.4433 gram CO_2 and 0.0337 gram H_2O.

	Calculated for $C_3HCl_2BrO_2$.	Found. I.	II.	III.
2Cl + Br	68.64	67.76	68.42	
C	16.36			16.66
H	.46			.52

In determining the solubility of this acid in cold water, a solution saturated at 20° was neutralised with baric carbonate, and the barium was determined in the filtered solution.

I. 6.0061 grams of a solution saturated at 20° gave 0.1523 gram $BaSO_4$.

II. 7.4519 grams of a solution saturated at 20° gave 0.1872 gram $BaSO_4$.

From these results the following percentages were calculated:

I.	II.
4.79	4.74

This acid is characterised by a series of well-defined salts, several of which were prepared for analysis.

Baric β-Bromdichloracrylate, $Ba(C_3Cl_2BrO_2)_2.3H_2O$.—The barium salt was made by neutralising the acid in aqueous solution with baric carbonate. It separated after concentration on the water bath in prismatic crystals, which were less soluble in cold than in hot water.

I. 1.3622 grams of the air-dried salt lost at 80° 0.1162 gram H_2O.

II. 1.2529 grams of the air-dried salt lost at 80° 0.1046 gram H_2O.

III. 0.5757 gram of the anhydrous salt gave 0.2353 gram $BaSO_4$.

	Calculated for $Ba(C_3Cl_2BrO_2)_2.3H_2O$.	Found. I.	II.
H_2O	8.58	8.53	8.35
	Calculated for $Ba(C_3Cl_2BrO_2)_2$.	III.	
Ba	23.82	24.03	

Calcic β-Bromdichloracrylate, $Ca(C_3Cl_2BrO_2)_2.3H_2O$.—The calcium salt separated in the form of rhombic plates sparingly soluble in cold water, when an aqueous solution of the acid was neutralised with calcic carbonate and concentrated on the water bath. For

analysis it was dried first at a constant weight in the air, then at 80°.

I. 1.2318 grams of the salt gave 0.1195 gram H_2O at 80°.

II. 1.1054 grams of the salt gave 0.1088 gram H_2O at 80°.

III. 0.9719 gram of the anhydrous salt gave 0.2741 gram $CaSO_4$.

	Calculated for $Ca(C_3Cl_2BrO_2)_2.3H_2O$.	Found. I.	II.
H_2O	10.15	9.71	9.85

	Calculated for $Ca(C_3Cl_2BrO_2)_2$.	III.
Ca	8.37	8.29

Potassic β-Bromdichloracrylate, $KC_3Cl_2BrO_2$.—The potassium salt was prepared by neutralisation of the acid with potassic carbonate. After concentrating the solution the salt separated in minute prismatic crystals, which were very soluble in water. When dried to a constant weight in the air, it lost nothing at 80°.

1.2362 grams of the salt dried at 80° gave 0.4144 gram K_2SO_4.

	Calculated for $KC_3Cl_2BrO_2$.	Found.
K	15.15	15.03

Argentic β-Bromdichloracrylate, $AgC_3Cl_2BrO_2$. — The silver salt was thrown down as a flocculent precipitate upon the addition of argentic nitrate to an aqueous solution of the acid. This salt is permanent in ordinary daylight, and it can be recrystallised from hot water without decomposition. It forms irregular rhombic plates, which are very slightly soluble in cold water.

0.6191 gram of salt dried over H_2SO_4 gave 0.2660 gram AgCl.

	Calculated for $AgC_3Cl_2BrO_2$.	Found.
Ag	33.03	32.34

Since β-dibromacrylic acid has been shown[1] to have the structure represented by the formula,

$$\begin{array}{l} CBr_2 \\ \| \\ CH \\ | \\ COOH, \end{array}$$

the chlorine addition-product would naturally have the form,

$$\begin{array}{l} CBr_2Cl \\ | \\ CHCl \\ | \\ COOH, \end{array}$$

[1] H. B. Hill, this Journal **4**, 273; and Proceedings Amer. Acad. **17**, 151.

and to the corresponding β-bromdichloracrylic acid must be assigned the formula,

$$\begin{array}{l} CBrCl \\ \| \\ CCl \\ | \\ COOH. \end{array}$$

XLIII.—ON ORTHOIODTOLUOLSULPHONIC ACID.

By Charles F. Mabery and George H. Palmer.

Hübner and Glassner[1] found that, when paraiodtoluol was dissolved in chloroform and treated with the calculated amount of sulphuric anhydride, two acids were formed, which they called α- and β-paraiodsulfitoluols. On trying the same reaction with orthoiodtoluol prepared from orthotoluidin by means of the diazo reaction, we were unable to effect any change in a chloroform solution, either in the cold or by the application of heat. But when sulphuric anhydride freshly distilled from Nordhausen sulphuric acid was added cautiously to the iodtoluol, at first keeping the mixture cold, and finally heating it for some time, the reaction was easily accomplished. To separate the resulting product from the acid mixture it was treated with an excess of baric carbonate, heated to boiling, filtered, and concentrated on the water bath. On cooling, the barium salt of orthoiodtoluolsulphonic acid separated in clusters of needles, which were much less soluble in cold than in hot water. So far as it could be determined by any difference in solubility or crystalline form of the barium salt, only one acid was formed. By precipitating carefully with sulphuric acid the barium from a solution of the barium salt, and concentrating the filtered solution on the water bath, the acid was left as an oily liquid, which did not solidify when cooled to 0°, or on long standing over sulphuric acid.

Baric Orthoiodtoluolsulphonate, $Ba(C_7H_6ISO_3)_2 . 1\frac{1}{2} H_2O$.—For analysis the barium salt was prepared as above described, and dried at first in the air, then at 100°.

I. 1.2312 grams of the air-dried salt lost 0.0407 gram H_2O at 100°.

II. 0.8011 gram of the air-dried salt lost 0.0300 gram H_2O at 100°.

[1] Berichte der deutschen chem. Gesellsch. **8**, 560.

III. 0.5967 gram of the anhydrous salt gave 0.1888 gram $BaSO_4$.

	Calculated for $Ba(C_7H_6ISO_3)_2.1\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	3.54	3.31	3.66
	Calculated for $Ba(C_7H_7ISO_3)_2$.		
Ba	18.61	18.03	

Calcic Orthoiodtoluolsulphonate, $Ca(C_7H_6ISO_3)_2.2\frac{1}{2}H_2O$.—This salt was prepared by neutralising the free acid with calcic carbonate, and evaporating the filtered solution on the water bath. The air-dried salt was heated to 100°.

I. 0.6243 gram of the air-dried salt lost 0.0414 gram H_2O at 100°.

II. 0.6250 gram of the air-dried salt lost 0.0424 gram H_2O at 100°.

	Calculated for $Ca(C_7H_6ISO_3)_2.2\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	6.62	6.61	6.78

0.7298 gram of the anhydrous salt gave 0.1762 gram $CaSO_4$.

	Calculated for $Ca(C_7H_6ISO_3)_2$.	Found.
Ca	6.31	7.10

Plumbic Orthoiodtoluolsulphonate, $Pb(C_7H_6ISO_3)_2.2H_2O$.—The lead salt was formed by treating the free acid with plumbic carbonate, filtering, and evaporating on the water bath. The air-dried salt lost two molecules of crystal water at 100°.

I. 1.2580 grams of the air-dried salt lost 0.0562 gram H_2O at 100°.

II. 1.2538 grams of the air-dried salt lost 0.0512 gram H_2O at 100°.

III. 0.7176 gram of the air-dried salt lost 0.0294 gram H_2O at 100°.

IV. 0.6163 gram of the anhydrous salt gave 0.2318 gram $PbSO_4$.

V. 0.6455 gram of the anhydrous salt gave 0.2425 gram $PbSO_4$.

	Calculated for $Pb(C_7H_6ISO_3)_2.2H_2O$.	Found. I.	II.	III.
H_2O	4.30	4.47	4.01	4.10
	Calculated for $Pb(C_7H_6ISO_3)_2$.	V.	VI.	
Pb	25.78	25.75	25.72	

An analysis of the free acid gave a percentage of iodine somewhat lower than the calculated value, but further study of it was prevented by the closing of the summer term.

ON THE ACTION OF BROMINE ON ANHYDROPROPIONYLPHENYLENDIAMINE.

By Erastus G. Smith.

The anhydrobase anhydropropionylphenylendiamine was first prepared and briefly described by Wundt (Berichte der deutschen chemischen Gesellschaft **11**, 829). The base has been prepared by the writer by another method, and several new salts of the same obtained. The method of preparation, and the preparation and analyses of the new salts, together with some corrections to those already described, are here given.

Ortho-nitro-propanilide, $C_6H_4\begin{cases}oNO_2\\INH.CO.CH_2.CH_3\end{cases}$.—If ortho-nitraniline ($C_6H_4.oNO_2.INH_2$. M. P. 71°) is treated with propionylchloride ($CH_3.CH_2.COCl$), a reaction follows even at ordinary temperatures, according to the formula:

M. P. 63° C.

$$C_6H_4\begin{cases}oNO_2\\INHH\end{cases} + ClOC.CH_2.CH_3 = C_6H_4\begin{cases}oNO_2\\INHCO.CH_2.CH_3\end{cases} + HCl.$$

The operation is best carried out as follows: The orthonitraniline is introduced into a short-necked flask with a standing tube, and somewhat more than the reckoned amount of the propionylchloride added. The reaction follows immediately, but it is best to warm gently to insure completeness. The fused mass is extracted with alcohol, and purified by recrystallisation to constant melting point. The ortho-nitro-propanilide thus obtained melts at 63°C. and crystallises from its solutions in large lemon-yellow crystals. It is soluble in boiling water, in alcohol, ether, and benzole.

Nitrogen Determination.—.1785 gram of the dried crystals yielded 21.6 cc. N at 7° C. and under 752 mm. pressure = 14.53 per cent. N.

	Reckoned.	Found.
$C_9H_{10}O_3$	85.55 per cent.	
N_2	14.43 "	14.53 per cent.

Anhydro-propionyl-phenylendiamine, $C_6H_4\begin{cases}N\\ \gtrless C.CH_2.CH_3.\\NH\end{cases}$—

M. P. 168° C.

If ortho-nitro-propanilide is treated with reducing agents, preferably tin and glacial acetic acid, this anhydrobase is formed. In the present case, at the close of the reaction the excess of tin was removed and the liquid poured into 5–6 volumes of water. The greater part of the tin was thus precipitated, and the remainder removed by sulphuretted hydrogen. The liquid was evaporated nearly to dryness and finally distilled in a small retort. For purification it is best to dissolve in hydrochloric acid and recrystallise. From this salt the pure base is precipitated by soda. The anhydropropionyl-phenylen-diamine is easily soluble in benzole, ether, alcohol, and boiling water, the solution from benzole depositing needle-shaped crystals. Its melting point is 168° C.

Analyses.

I. .2005 gram of the base yielded 33.1 cc. N at 10.5° C. and under 753.5 mm. pressure = 19.56 per cent. N.

II. .3771 gram of the dry base yielded 1.035 grams CO_2 = 74.16 per cent. C, and .2335 gram H_2O = 6.88 per cent. H.

	Reckoned.	Found.
C_9	73.97 per cent.	74.16 per cent.
H_{10}	6.84 "	6.88 "
N_2	19.17 "	19.56 "

The base gives a series of well crystallising salts, *none of them containing water of crystallisation.*[1]

I. *Hydrochloric Acid Salt,* $C_6H_4\begin{cases}N\\ \gtrless C.CH_2.CH_3\\ NH_2Cl\end{cases}$.—If the anhydrobase is dissolved in water and HCl added, the solution yields by evaporation long colorless crystals of the hydrochloric acid salt *without water of crystallisation.*

Analysis.

.1064 gram of the salt yielded .0841 gram Ag_2Cl_2 = 19.54 per cent. Cl.

	Reckoned.	Found.
$C_6H_{11}N_2$	80.53 per cent.	
Cl	19.45 "	19.54 per cent.

II. *Platinum Chloride Double Salt,*

$$\left[C_6H_4\begin{cases}N\\ \gtrless C.CH_2.CH_3\\ NH_2Cl\end{cases}\right]_2 PtCl_4.$$

[1] Ber. d. chem. Ges. **11**, 899.

If to the solution of the hydrochloric acid salt, platinum chloride is added in excess, the solution yields on evaporation bright orange red crystals of the platinum chloride double salt. *These crystals contain no water of crystallisation.*

Analyses.

I. .3374 gram of the salt yielded on ignition .0944 gram = 27.98 per cent. Pt.

II. From 1.14885 grams of the salt the platinum precipitated as PtS_2 and ignited, gave .3211 gram = 27.93 per cent. Pt.

	Reckoned.	Found. I.	II.
$C_{18}H_{22}N_4Cl_2Cl_4$	72.26 per cent.		
Pt	27.73 "	27.98 per cent.	27.93 per cent.

III. *Mercuric Chloride Double Salt,*

$$\left[C_6H_4\begin{cases}N\\ \gg C.CH_2.CH_3\\ NH_2Cl\end{cases}\right]; HgCl_2.$$

If mercuric chloride is added to the hydrochloric acid salt and the solution evaporated, the mercuric chloride double salt crystallises out in long colorless needles.

Analysis.

.516 gram of the salt yielded with sulphuretted hydrogen .2864 gram HgS = 44.19 per cent. Hg.

	Reckoned.	Found.
$C_6H_{11}N_2Cl_3$	55.74 per cent.	
Hg	44.15 "	44.19 per cent.

IV. *Pyrochromic Acid Salt,*

$$\left[C_6H_4\begin{cases}N\\ \gg C.CH_2.CH_3\\ NH\end{cases}\right]_2; H_2Cr_2O_7.$$

If about two grams of the base are dissolved in sulphuric acid and $K_2Cr_2O_7$ added, this salt is obtained on evaporating the solution.

Analysis.

.1683 gram of the salt gave .0511 gram Cr_2O_3 = 20.79 per cent. Cr.

	Reckoned.	Found.
$C_{18}H_{22}N_4O_7$	79.45 per cent.	
Cr_2	20.54 "	20.79 per cent.

The Action of Bromine on Anhydropropionylphenylendiamine.

It is possible by this action to effect, either:

a. The substitution of bromine for hydrogen in the phenylene group (C_6H_4), or:

b. An oxidation whereby the anhydrobase can be changed to a carboxyl compound, or:

c. Both reactions could simultaneously occur.

It will be shown that the bromine substitutions are undoubtedly effected. And from investigations yet in progress there are strong reasons for believing that by the continued action of bromine an oxidation of the bromine bases actually takes place. The treatment with the bromine is as follows:

Twenty grams of the pure anhydrobase are dissolved in two litres of hot water, and, after cooling, diluted bromine water is added in small portions until the color of the bromine water after standing twelve hours is distinctly permanent. A heavy, difficultly soluble, flocculent precipitate is formed. What has dissolved can be advantageously precipitated by sodium acetate and the whole filtered and well washed with *cold* water. The white mass thus obtained is dissolved in alcohol and allowed to crystallise. At first thick yellow crystals separate, and after longer standing, *long colorless needles* appear. Immediately on their appearance the mother liquor is filtered off and the crystals washed with dilute alcohol, and finally with a little dilute hydrochloric acid and cold water. The further treatment must proceed in two parts:

a. The alcoholic mother liquor.

b. The insoluble crystals.

a. To the alcoholic mother liquor is added an excess of hydrochloric acid and the whole evaporated on the water bath. On standing the hydrochloric acid salt of the base anhydro-propionyl-di-bromine-phenylen-diamine crystallises out.

b. The insoluble crystals when boiled with barium hydroxide are partially dissolved. The insoluble portion is filtered off and dissolved in alcohol. After again filtering to free from traces of barium carbonate, the solution yields on evaporation the nearly pure crystalline base anhydro-propionyl-tri-bromine-phenylen-diamine. The portion soluble in barium hydroxide is evaporated with hydrochloric acid to dryness, and extracted with alcohol. This alcoholic extract evaporated, redissolved in water and treated with sodium acetate, gives a precipitate crystallising well from

alcohol. This appears to possess the properties of an acid, but has not yet been fully investigated.

Anhydropropionyl-di-bromine-phenylen-diamine,

$$C_6H_2Br_2\begin{cases} N \\ \gg C.CH_2.CH_3.— \\ NH \end{cases}$$

M. P. 224–226° C.

The hydrochloric acid salt described above (*a*) is thrice recrystallised and the pure base precipitated with ammonia. The white flocculent precipitate is difficultly soluble even in boiling water, but dissolves readily in benzole, ether, *dilute* alcohol and *strong caustic soda*. The crystals from alcohol melt at 224–226° C. The complete analysis will be given below under the nitric acid salt.

Nitric Acid Salt, $C_6H_2Br_2\begin{cases} N \\ \gg C.CH_2.CH_3.— \\ NH_2ONO_2 \end{cases}$ A gram of the pure base dissolved in water and treated with nitric acid yields on evaporation crystals of the nitric acid salt. These are especially fine and well adapted for complete analysis to fully establish the composition of the base.

Analyses.

I. .1745 gram of the salt gave 17.6 cc. N at 16° C. and under 747 mm. pressure = 11.55 per cent. N.

II. .1795 gram of the salt yielded .0447 gram H_2O = 2.73 per cent. H, and .1924 gram CO_2 = 29.23 per cent. C.

III. .192 gram of the salt heated to 180° C. with HNO_3 and silver nitrate gave .1989 gram Ag_2Br_2 = 44.04 per cent. bromine.

	Reckoned.	Found.
C_9	29.42	29.23
H_9	2.45	2.73
Br_2	43.59	44.04
N_3	11.44	11.55
O_2	13.08	

Hydrochloric Acid Salt, $C_6H_2Br_2\begin{cases} N \\ \gg C.CH_2.CH_3; H_2O.— \\ NH_2Cl \end{cases}$

This salt is obtained in long acicular crystals, as already given in the preparation of the base.

Analyses.

I. The salt contains one molecule of water of crystallisation.

The water cannot however be expelled without decomposing the salt. .7232 gram remained constant at 152° C. Between 152–155° the salt is decomposed.

II. .21975 gram of the salt gave .084 gram Ag_2Cl_2 = 9.45 per cent. Cl.

III. .20515 gram of the salt gave .0792 gram Ag_2Cl_2 = 9.51 per cent. Cl.

IV. .1739 gram of the salt gave .07009 gram Ag_2Cl_2 = 9.96 per cent. Cl.

	Reckoned.	Found. I.	II.	III.
$C_9H_9Br_2N_3;H_2O$	90.09 per cent.			
Cl	9.90 "		9.45 per ct.	9.51 per ct. 9.96 per ct.

Platinum Chloride Double Salt,

$$\left[C_6H_3Br_3\begin{cases}N\\ \gtrless C.CH_2.CH_3\\ NH_2Cl\end{cases}\right]_2PtCl_4.$$

A gram of the hydrochloric acid salt dissolved in water and platinum chloride added, gives fine orange-red crystals of the platinum double salt.

Analysis.

From .1935 gram of the salt the platinum precipitated as PtS_2 and ignited, gave .0358 gram = 19.04 per cent. Pt.

	Reckoned.	Found.
$C_{18}H_{18}Br_4N_4Cl_2Cl_4$	80.90 per cent.	
Pt	19.09 "	19.04 per cent.

Anhydropropionyl-tri-bromine-phenylen-diamine,

$$C_6HBr_3\begin{cases}N\\ \gtrless C.CH_2.CH_3.\\ NH\end{cases}$$

M. P. 257–262° C.

The preparation of this base has been already given under *b*. The pale yellow granular crystals are difficultly soluble in alcohol, ether, benzole, and hot water. Crystals from alcohol melt at 257–262° C.

Analyses.

I. .2126 gram of the base gave 14 cc. N at 25° C. and under 751 mm. pressure = 7.25 per cent. N.

II. .1013 gram of the crystals gave .1031 gram $CO_2 = 27.75$ per cent. C, and .0286 gram $H_2O = 3.06$ per cent. N.

III. .1804 gram of the base gave (when heated to 180° C. with nitric acid and silver nitrate) .2166 gram $Ag_2Br_2 = 62.86$ per cent. Br.

	Reckoned.	Found.
C_9	28.19	27.75
H_7	1.82	3.06
N_2	7.31	7.25
Br_2	62.63	62.86

Hydrochloric Acid Salt, $C_6HBr_3 \begin{cases} N \\ \gtrless C.CH_2.CH_3 ; 2H_2O. \\ NH_2.Cl \end{cases}$ — If the base is dissolved in dilute hydrochloric acid and the solution evaporated, this salt is obtained in small transparent crystals.

Analyses.

I. .1227 gram of the air-dried crystals lost at 100° .009 gram = 7.33 per cent. H_2O.

	Reckoned.	Found.
$C_9H_7Br_3N_2, HCl$	92.09 per cent.	
H_2O	7.90 "	7.33 per cent.

II. .114 gram of the anhydrous salt yielded .0942 gram Ag_2Cl_2 = 8.26 per cent. Cl.

	Reckoned.	Found.
$C_9H_7Br_3N_2, H$	91.53 per cent.	
Cl	8.46 "	8.26 per cent.

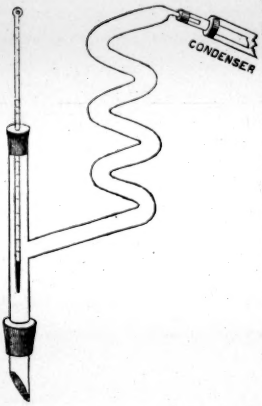
CHEMICAL LABORATORY OF BELOIT COLLEGE, *Beloit, Wisconsin.*

NEW FORMS OF LABORATORY APPARATUS.

BY EDWARD HART.

I.—*Apparatus for Fractional Distillation.*

The apparatus has the form shown in the figure. The bent tube before bending should be at least 2 feet long, but may be of any



length with a corresponding number of bends (the greater the length, the more perfect the separation), and an internal diameter of at least $\frac{3}{8}$ inch. The principle is the familiar one of the "dephlegmator." The condensed portion here runs down, and at each bend passes around the inside of the tube, the vapor passing upward through the ring of descending liquid. A comparison with a Le Bel and Henniger tube[1] with 4 bulbs showed very little difference in the rate of separation. The apparatus is preferable to that of Le Bel and Henniger by reason of its simplicity and small cost. It can be made by an amateur glassblower, while the former can be made only by a skilled workman.

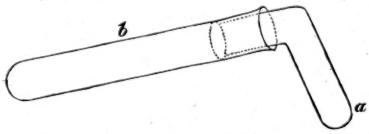
II.—*A Valve for use in Standardising Permanganate.*

The valve shown has been in use for several years in this laboratory, and proves perfectly satisfactory. The trouble with the old forms (in one of which a slit is made in the side of a rubber tube, and in the second, a piece of rubber is pinned over a hole in a cork, and this slipped over a tube leading from the flask) is that however carefully they are made, they get out of order very soon and become a nuisance. The liquid in the flask is rapidly heated as soon as the iron wire is introduced, and as soon as the wire is dissolved, boiled to expel all air, and the tube pushed down so that the opening *a* in the tube is inside the opening of the rubber cork, which prevents the air from flowing back into the flask as it cools. The tube is closed at *b*. The opening *a* is made either by filing crosswise with a rat-tail file, or better, by heating with a pointed flame and blowing an opening in the side of the tube.

[1] Berichte d. deut. chem. Ges. **7**, 1084.

III.—*A Retort and Receiver for small Distillations.*

It is oftentimes inconvenient to use a retort in making small distillations, chiefly because it takes considerable time to fit up a retort stand. For such small distillations as the preparation of chlorochromic acid in testing for chlorine, the following arrangement is convenient:



The retort tube *a* is made by bending a 6 inch test tube. If the tube is heated to redness and blown into while bending, a neat and strong bend is easily made. In use, the receiver tube *b* is held in the hand while the retort tube is placed above a small flame. For a retort tube made from a 4 inch test tube, a 6 inch test tube makes a receiver of the proper size. For a 6 inch retort tube an 8 inch test tube is needed.

LAFAYETTE COLLEGE, *April*, 1884.

ON A NEW CLASS OF COMPOUNDS ANALOGOUS TO THE PHTHALEINS.

BY IRA REMSEN.

The analogy in constitution between phthalic and ortho-sulphobenzoic acids suggested that the latter might act upon phenols in the same way that the former does, and that thus compounds analogous to the phthaleins might be obtained. Experiment showed that this thought is well founded. A mixture of about equal parts of pure potassium ortho-sulphobenzoate and resorcin was brought into a dry test-tube with a small quantity of concentrated sulphuric acid, and the whole gently heated for a few minutes. A drop of the resulting dark-colored liquid was dissolved

in a test-tube full of water and a little caustic soda added, when a fluorescence fully equal to that caused by ordinary fluorescein was observed. By transmitted light the color of the solution is somewhat redder than that of fluorescein, but in other respects they can hardly be distinguished from one another. The same reaction takes place and with the same ease, when instead of the salt of ortho-sulphobenzoic acid, the imide derivative, benzoic sulphinide, $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH$, is used.

Substitution products of ortho-sulphobenzoic acid act in the same way. The experiment has been tried with nitro-ortho-sulphobenzoic acid, $C_6H_3\begin{cases}COOH\\SO_2OH\ (o)\\NO_2\ (p)\end{cases}$, readily obtained by oxidising the corresponding nitro-toluenesulphonic acid, and brom-ortho-sulphobenzoic acid, $C_6H_3\begin{cases}COOH\\SO_2OH\ (o)\\Br\ (p)\end{cases}$, obtained from brom-toluenesulphonic acid.

It is probable that the simplest phthalein prepared in this way will be found to bear to phenol-phthalein the relation indicated by these formulas:

$$\begin{matrix}\begin{cases}C_6H_4OH\\C_6H_4OH\\C_6H_4.CO\end{cases}\\|\\O\text{———}\perp\end{matrix}\qquad\text{and}\qquad\begin{matrix}C\begin{cases}C_6H_4OH\\C_6H_4OH\\C_6H_4.SO_2\end{cases}.\\|\\O\text{———}\perp\end{matrix}$$

The compounds may appropriately be designated as *sulphon-phthaleins*, which distinguishes them from the normal phthaleins of Baeyer and the thio-phthaleins the formation of which from thio-phthalic anhydride, $C_6H_4<\begin{matrix}CO\\CS\end{matrix}>O$, and the phenols has been made probable by the experiments of Graebe.[1]

Experiments, which it is hoped will lead to a more definite knowledge of the sulphon-phthaleins, have been undertaken in this laboratory. As, on account of the vacation, nothing more can be done on the subject until next fall, I have thought it desirable at this time to call attention to the reaction. Should it prove possible to isolate the new bodies, I propose, with the aid of some of my younger colleagues, to make an exhaustive study of them.

[1] Berichte der deutschen chemischen Gesellschaft **17**, 1177.

THE DECOMPOSITION OF SULPHONIC ACIDS BY HEATING WITH HYDRATED SULPHURIC ACID.

By C. Friedel and J. M. Crafts.

Messrs. Armstrong and Miller give, in the last numbers of the *Journal of the Chemical Society*, a method for regaining aromatic hydrocarbons from their sulphonic acids, by distilling these latter, mixed with sulphuric acid more or less diluted, in a current of steam, or by heating the mixture in sealed tubes at various temperatures.

They have also succeeded in separating certain hydrocarbons by taking advantage of the differences of temperature at which their sulphonic acids are decomposed.

This publication leads us to speak of experiments in the same direction which entirely confirm the observations of these authors, and bear witness to the great convenience of their method. We have employed, for two years past, exactly the same process for decomposing the sulphonic acids of a class of bodies which cannot be separated from that combination by hydrochloric acid; namely, the sulphonic acids of the hydrides of naphthalene. The publication of the results was, however, delayed, because these compounds were found to present not only this difficulty, for their isolation in a state of purity, but also the more serious one of being readily oxidisable in the air,[1] and this latter property has prevented us

[1] In the month of September of last year, one of us communicated to Professor Graebe the fact of the easy oxidation in the air of the tetrahydride of naphthalene, obtained by the decomposition of naphthalene with chloride of aluminium. Graebe had taken up the study of the tetrahydride formed by the action of iodhydric acid upon naphthalene, but he was not aware at that time that this body was oxidisable in the air, and thought the tetrahydrides formed in these two reactions might be distinct bodies. He has since published, together with Mr. Guye (Chem. Gesell., Dec. 1883), some observations upon this subject, which show that in this respect there is no distinction between the hydrides of naphthalene formed by the chloride of aluminium or by the iodhydric acid process, but it still remains to be seen whether the two products are really identical.

The tetrahydride of naphthalene, which we had in hand, was found to form at least two sulphonic acids, but they are oxidisable in the air, as well as their salts, in aqueous solution; and the solubility of the salts is seen to change rapidly when their solutions are exposed to evaporation. In order, therefore, to get their true coefficient of solubility, it will be necessary to evaporate them in an atmosphere of an inert gas.

It is impossible to make a comparison with the sulpho salt of the acid studied by Messrs. Graebe and Guye, as they give no determinations of solubility. The principal product, which can be obtained by treatment with hydrated sulphuric acid after such an oxidation, is naph-

thus far from being able to obtain salts of these acids in a satisfactory condition. The study of these substances is in progress, and we had intended to publish an account of the mode of decomposition of their sulphonic acids as part of a paper upon the hydrides of naphthalene and other bodies which can be obtained by decomposing naphthalene with chloride of aluminium, but as the results are incomplete, we will speak of the interesting decompositions of the sulphonic acids which we have observed.

The tetrahydride of naphthalene combines very readily with strong sulphuric acid at the ordinary temperature, with considerable disengagement of heat, and the resultant sulphonic acid is a very stable body. It only begins to be decomposed by heating with chlorhydric acid at 185°, and at this temperature, decomposition takes place, and the products formed are naphthalene and sulphuretted hydrogen mixed with more or less of the hydride. The reduction of sulphuric acid by a hydrocarbon of this class has, we believe, not hitherto been observed.

It was in order to avoid this decomposition that we adopted the expedient, at first, of heating the sulphonic acid or its salt in sealed tubes, in an essence of turpentine bath (157°), with a mixture of sulphuric acid and various proportions of water, from one half to three times the weight of the sulphuric acid. Total decomposition is effected in about 12 hours, and no oxidation takes place. The rapidity of the decomposition increases, within certain limits, with the strength of the sulphuric acid; an aqueous solution of the sulphonic acid, for instance, is entirely stable when heated at 157°. The range of temperature appeared to be from about 145° to 160°, at which sulphuric acid of the different strengths mentioned decomposed the hydride of naphthalene sulphonic acid.

We worked with large quantities, more than a kilogram, of hydride of naphthalene, and in many cases found it more convenient to use exactly the process of distillation with steam which

thalene, and on decomposing the sulphonic acids at any stage, mixtures of hydride of naphthalene and of naphthalene were the only bodies obtained.

The hydrocarbon itself, when exposed several months in a loosely corked flask, absorbs oxygen and undergoes a transformation similar to that of essence of turpentine under like circumstances. When afterwards heated to near its boiling point, an active reaction sets in with considerable disengagement of heat, water is formed, and a series of hydrocarbons pass, distilling within a great range of temperatures.

An oxidised tetrahydride of naphthalene is resinefied by strong sulphuric acid in the same manner as essence of turpentine, while the pure tetrahydride dissolves in sulphuric acid without change of color. This difference offers a good test for the detection of oxidation.

has been so well studied by Messrs. Armstrong and Miller. Here, it suffices to mix the sulphonic acid, or a salt, with three or four times its weight of sulphuric acid, diluted with about one third part of water, to put a thermometer in the liquid, and to heat the retort, passing steam through the liquid, up to the point at which the hydrocarbon begins to be given off, the temperature, of course, rising with the concentration of the acid in the retort. At any desired point it is very easy to regulate the flame so as to maintain a constant temperature, and to continue the operation for several hours to insure complete decomposition at a known temperature. Under these circumstances, decomposition begins to be active at about 160°, and the temperature can be pushed to 175° or 180° without noticeable oxidation of the hydrocarbon.

We used this method to effect the separation of naphthalene and hydride of naphthalene, which is very difficult by distillation alone. The sulphonic acid of naphthalene is more readily decomposed than that of the hydride, and on heating at 160°, most of the naphthalene passes with the first portions of the distillate. The separation, however, is never complete.

We also studied a similar reaction with regard to the sulphonic acids of benzene and its homologues, and noticed, as Messrs. Armstrong and Miller have done, differences of stability of the different aromatic hydrocarbons; but in the case in which we wished particularly to apply it, viz. for the purification of pentamethylbenzene from the durols and from hexamethylbenzene, an obstacle presented itself in the difficulty of forming a sulphonic acid from the pentamethylbenzene.

It is evident there can be no question of the priority of the publication of Messrs. Armstrong and Miller, and we only desire to add to the facts which they have stated, this description of the application of their reaction to the case of the hydrides of naphthalene, which we have been studying independently for some time.

PARIS, *June* 12, 1884.

ON CASSITERITE FROM IRISH CREEK, ROCKBRIDGE CO., VIRGINIA.

By W. G. Brown.

The cassiterite at this locality is found as loose crystals and fragments, on the surface and in veins, in place.

The tin-bearing veins, which have been followed to a depth of from 12 to 20 feet, in the course of the "prospecting" which is now being carried on, occur in a coarse-grained, very much decomposed granite or gneiss, which does not contain more than a trace of tin. They run northeast to southwest conformably with the common strike of the rocks of the Blue Ridge, or in a direction nearly at right angles to this.

The cassiterite is found in the closest connection with quartz; frequently one or the other mineral, or a mixture of both, filling the fissure, with or without a definite arrangement. In some places the vein is wholly quartz, which passes into a quartz, with imbedded crystals of cassiterite; the cassiterite increasing, the quartz is sometimes enclosed as a band between two bands of cassiterite, finally the quartz is entirely replaced.

Along with the cassiterite, wolframite is found in rough crystals or irregular masses, on which an occasional crystal face is seen, mixed with the products of its disintegration, in all stages of weathering, from the almost fresh unchanged mineral to red ochre or to limonite, with only a trace of manganese. In some specimens the cassiterite is wholly imbedded in these decomposition products.

A light-colored mica, in small tables, almost invariably accompanies the cassiterite. Usually upon that portion of the vein next to the "country rock" there is a layer of this mica, or the tin-stone is banded on each side with a layer of the decomposition products of the wolframite, and then on these the mica is found. Its composition has not yet been determined.

An auriferous mispickel is found sparingly in the vein, and a hexagonal mineral which may have resulted from the alteration of beryl.

The veins of cassiterite, which are crystalline, vary in thickness from ½ inch or less to 3 or 4 inches, with an occasional mass of

much larger dimensions. They may be solid, or may contain cavities which are lined with prismatic crystals of cassiterite up to an inch in length, and these crystals are at times covered with red ochre or with a layer of iridescent, globular limonite, or the cavities may be filled with the decomposition products of the wolframite. On breaking the apparently solid vein tin-stone the interlocking crystals often separate, sharply defined, from each other. The vein tin passes in color from brownish white through various shades of brown to reddish brown, with a dull, subresinous or adamantine lustre. Subtranslucent to opaque. It shows only traces of cleavage. Fracture even. Sp. gr: 6.536.

The crystals found thus far are comparatively dull; only very few have approached the lustre and beauty of those of Saxony and Bohemia. One of these, a compound crystal, varies from wax yellow through brown to black in color. Translucent. Resinous to adamantine lustre. Splendent. Subconchoidal to uneven fracture. Sp. gr. 6.609.

A few simple crystals are found. One a combination of the following forms, 111 (P), 110 (∞P), 100 (∞P∞), 101 (P∞). Another implanted shows the base, the combination being 111 (P), 110 (∞P), 100 (∞P∞), 210 (∞P2), 101 (P∞); 001 (0P). On a broken crystal 110 (∞P), 210 (∞P2).

The angle between 111 (P), 001 (0P) was measured with a reflective goniometer, and found to be 136° 10′, but owing to the imperfect reflection from the faces, it was only possible to obtain this approximate result by placing small pieces of thin glass on the planes. Twinned crystals are quite common. Twinning plane 101 (P∞). In many crystals the twinning is repeated. One compound crystal is twinned upon each of the 101 (P∞) planes at one end, and these second crystals are again twinned, meeting from opposite angles over the centre of the principal crystal.

Most of the crystals are striated on 110 (∞P) parallel to the edge 110 (∞P), 100 (∞P∞). Besides this striation there are striations on 110 (∞P) parallel to the edge 110 (∞P), 101 (P∞). These lines are very sharp and distinct, covering 110 (∞P) with rhomboidal markings. Although at times somewhat difficult to see with the unaided eye, these striations, which are more noticeable on the dull than on the bright crystals, are more readily observed and are more characteristic than the first mentioned. They serve well as an indicator of the prism of the first order in determining compound crystals.

The cassiterite was analysed[1] by reducing at a low red heat the very finely pulverised mineral, placed in a porcelain boat in a stream of dry hydrogen. The reduction of nearly two grams was complete in about 45 minutes. The reduced mass treated with hot, strong hydrochloric acid left an insoluble residue which was ignited and weighed. This residue was treated repeatedly with hydrofluoric acid and the silica volatilised as silicon fluoride. The remaining fixed residue, which was proved to contain neither alumina, tungstic acid, nor titanic acid, is considered tantalic acid. In the hydrochloric acid solution, which was colorless, thus showing the absence of tungstic acid, the tin was separated as stannous sulphide, and the remaining constituents separated and determined in the usual way. It may be mentioned that the tendency of the stannous sulphide to run through the filter was prevented by the addition to the wash-water of a little ammonium nitrate.

The analysis gave:

SnO_2	94.895
SiO_2	.760
Ta_2O_5	.237
Fe_2O_3	3.418
CaO	.244
MgO	.027
Ignition	.385
	99.966

UNIVERSITY OF VIRGINIA, *June*, 1884.

Contributions from the Chemical Laboratory of Harvard College.

XLIV.—ON MUCOPHENOXYBROMIC ACID.[2]

BY HENRY B. HILL AND EDWARD K. STEVENS.

The products which are formed when mucobromic acid is treated with a large excess of baric hydrate, have already been de-

[1] Becke, Zeit. f. Krystal. 1878, II, S. 318, and Rammelsberg, Leit. f. d. quant. chem. Analyse, 1874, S. 68.

[2] Proceedings American Acad. Arts and Sciences.

scribed by O. R. Jackson and one of us.[1] Formic and dibromacrylic acids were found to be the first products of this reaction, although even in the cold a part of the dibromacrylic acid was further converted into brompropiolic acid. Later experiments undertaken with the view of avoiding this secondary decomposition, showed that an entirely different reaction ensued when the conditions were so modified that the solution was at no time strongly alkaline. The chief product formed in this case was easily found to be an acid containing four atoms of carbon and one of bromine; but the determination of its constitution proved to be a matter of more difficulty, and a description of it must therefore be postponed until it can be further studied. Since it seemed possible that sodic ethylate or potassic phenylate might react upon mucobromic acid and yield similar products, whose constitution could more easily be determined, we turned our attention in this direction. Although we have been unable to obtain any such products by the action of sodic ethylate, potassic phenylate has given us well-defined products containing the phenoxyl group.

Mucophenoxybromic Acid.

Potassic phenylate acts upon potassic mucobromate in aqueous solution at ordinary temperatures; but the isolation of the potassic mucophenoxybromate thus formed is somewhat difficult, and we have not been able to obtain uniform results in our various preparations. We have found it advantageous to use a large excess of potassic phenylate, and to add also potassic hydrate in quantity sufficient to neutralise the mucobromic acid taken. We usually have dissolved 25 grams of crystallised phenol and 17.5 grams of ordinary potassic hydrate in 30 grams of water, and after the solution is well cooled, have added 20 grams of mucobromic acid. After the lapse of a short time small compact rhombic crystals of the new potassium salt begin to separate, and the reaction is ordinarily completed in less than an hour. The crystals should then be collected at once, drained by the pump, and washed with a little cold water. Hydrochloric acid added to an aqueous solution of the salt then precipitates mucophenoxybromic acid in clustered needles, which, when dried over sulphuric acid, gave the following results:

[1] This Journal **3**, 106; and Proc. Amer. Academy of Arts and Sciences **16**, 188.

I. 0.2156 gram substance gave on combustion 0.3486 gram CO_2 and 0.0525 gram H_2O.

II. 0.2250 gram substance gave 0.1564 gram AgBr.

III. 0.2168 gram substance gave 0.1504 gram AgBr.

	Calculated for $C_4H_2(OC_6H_5)BrO_3$.	Found. I.	II.	III.
C	44.28	44.11		
H	2.58	2.71		
Br	29.52		29.58	29.52

When crystallised from hot water, mucophenoxybromic acid forms small flat prisms concentrically grouped, which melt at 104–105°. The acid is readily soluble in hot water, sparingly in cold; readily soluble in alcohol or ether, soluble in hot benzol or chloroform, and almost insoluble in carbonic disulphide or ligroin. An aqueous solution of the acid reduces silver oxide on warming, and gives with ferric chloride a whitish precipitate.

Potassic Mucophenoxybromate. $KC_4H(OC_6H_5)BrO_3$. The salt obtained by the action of potassic phenylate upon mucobromic acid was recrystallised several times from warm water. It formed then oblique tabular crystals quite soluble even in cold water. The salt is more stable in aqueous solution than the corresponding mucobromate, and yet suffers quite rapid decomposition at temperatures near 100°. The salt dried by exposure to the air contains no water of crystallisation.

I. 0.4314 gram of the salt gave on ignition with H_2SO_4 0.1227 gram K_2SO_4.

II. 0.4430 gram of the salt gave on ignition with H_2SO_4 0.1255 gram K_2SO_4.

	Calculated for $KC_4H(OC_6H_5)BrO_3$.	Found. I.	II.
K	12.65	12.76	12.72

Baric Mucophenoxybromate. $Ba(C_4H(OC_6H_5)BrO_3)_2 3H_2O$. This salt was obtained by neutralising a cold aqueous solution of the acid with baric carbonate, and allowing the solution thus obtained to evaporate spontaneously. It separated in leafy rhombic crystals, which were very soluble in water. On warming the solution decomposition ensued. The air-dried salt contained three molecules of water, one of which it lost over sulphuric acid, the rest at 100°.

I. 0.8147 gram of the air-dried salt lost over H_2SO_4 0.0213 gram H_2O, and in addition 0.0403 gram at 100°.

II. 0.7863 gram of the air-dried salt lost over H_2SO_4 0.0201 gram H_2O, and in addition 0.0397 gram at 100°.

	Calculated for $Ba(C_4H(OC_6H_5)BrO_3)_2.3H_2O$.	Found. I.	II.
H_2O	2.46	2.61	2.56
$3H_2O$	7.39	7.56	7.61

0.4628 gram of the salt dried at 100° gave on ignition with H_2SO_4 0.1599 gram $BaSO_4$.

	Calculated for $Ba(C_4H(OC_6H_5)BrO_3)_2$.	Found.
Ba	20.23	20.32

When treated with an excess of an alkaline hydrate, mucophenoxybromic acid, like mucobromic, is decomposed, and yields a substituted acrylic acid together with formic acid.

Phenoxybromacrylic Acid.

We have found it most convenient to dissolve equal weights of potassic hydrate and potassic mucophenoxybromate each in their own weight of water, and to mix the hot solutions. On cooling, potassic phenoxybromacrylate separates in well-formed crystals. From these, by the addition of hydrochloric acid, we prepared the acid which, when recrystallised from hot water and dried over sulphuric acid, gave the following results:

I. 0.2037 gram of the substance gave on combustion 0.3307 gram CO_2 and 0.0553 gram H_2O.

II. 0.2027 gram of the substance gave 0.1577 gram AgBr.

III. 0.2238 gram of the substance gave 0.1739 gram AgBr.

	Calculated for $C_3H_2(OC_6H_5)BrO_2$.	I.	Found. II.	III.
C	44.44	44.27		
H	2.88	3.02		
Br	32.93		33.11	33.07

Phenoxybromacrylic acid crystallises from hot water in long silky needles, which melt at 138°. It is almost insoluble in cold water, and is somewhat sparingly soluble even in boiling water. In ether or alcohol it is very soluble; in chloroform or benzol it dissolves on

warming, and crystallises as these solutions cool. Carbonic disulphide dissolves it with more difficulty.

Potassic Phenoxybromacrylate. $KC_8H(OC_6H_5)BrO_2$. On cooling the hot solution of potassic mucophenoxybromate in potassic hydrate, potassic phenoxybromacrylate separates in well-formed rhombic plates, which may be recrystallised from hot water, although they are quite soluble even in cold water. The air-dried salt proved to be anhydrous.

I. 0.5073 gram of the air-dried salt gave on ignition with H_2SO_4 0.1588 gram K_2SO_4.

II. 0.5077 gram of the air-dried salt gave on ignition with H_2SO_4 0.1572 gram K_2SO_4.

	Calculated for $KC_8H(O_6H_5)BrO_2$.	Found. I.	II.
K	13.91	14.06	13.90

Baric Phenoxybromacrylate. $Ba(C_8H(OC_6H_5)BrO_2)_2.5H_2O$. On neutralising a boiling solution of the acid with baric carbonate, and evaporating on the water-bath, the barium salt was obtained in the form of radiating prisms, which were permanent in the air and hardly lost in weight over sulphuric acid. It was freely soluble in cold water. The air-dried salt gave on analysis:

I. 1.2120 gram of the air-dried salt lost at 110° 0.1535 gram H_2O.

II. 1.0468 gram of the air-dried salt lost at 110° 0.1345 gram H_2O.

III. 0.6687 gram of the air-dried salt lost at 110° 0.0855 gram H_2O.

	Calculated for $Ba(C_8H(OC_6H_5)BrO_2)_2.5H_2O$.	I.	Found. II.	III.
H_2O	12.66	12.67	12.85	12.78

0.5017 gram of the salt dried at 110° gave on ignition with H_2SO_4 0.1873 gram $BaSO_4$.

	Calculated for $Ba(C_8H(OC_6H_5)BrO_2)_2$.	Found.
Ba	22.06	21.95

Calcic Phenoxybromacrylate. $Ca(C_8H(OC_6H_5)BrO_2)_2.5H_2O$. The calcium salt was prepared from the acid by neutralising its aqueous solution with calcic carbonate. It was readily soluble in water, and crystallised on cooling its concentrated solution in clustered needles, which were permanent in the air or over sulphuric acid.

I. 0.9361 gram of the air-dried salt lost at 100–105° 0.1381 gram H_2O.

II. 0.7563 gram of the air-dried salt lost at 100–105° 0.1122 gram H_2O.

	Calculated for $Ca(C_3H(OC_6H_5)BrO_2)_2.5H_2O$.	Found. I.	II.
H_2O	14.66	14.75	14.84

0.5046 gram of the salt dried at 100–105° gave on ignition with H_2SO_4 0.1310 gram $CaSO_4$.

	Calculated for $Ca(C_3H(OC_6H_5)BrO_2)_2$.	Found.
Ca	7.64	7.64

Argentic Phenoxybromacrylate. $AgC_3H(OC_6H_5)BrO_2$. The silver salt may be precipitated by the addition of argentic nitrate to a hot aqueous solution of the acid. It crystallises in needles which may be recrystallised without decomposition from boiling water. When dried over sulphuric acid, the salt gave the following results:

I. 0.4464 gram of the salt gave on precipitation with HBr 0.2391 gram AgBr.

II. 0.4240 gram of the salt gave on precipitation with HBr 0.2268 gram AgBr.

	Calculated for $AgC_3H(OC_6H_5)BrO_2$.	Found. I.	II.
Ag	30.85	30.77	30.72

Phenoxybromacrylic acid is therefore one of the products formed from mucophenoxybromic acid by the action of potassic hydrate. The mother liquors from which the potassic phenoxybromacrylate had crystallised yielded on acidification with dilute sulphuric acid and distillation an acid distillate, which gave with ferric chloride and bromine water reactions showing the presence of small quantities of phenol. When neutralised with calcic carbonate and evaporated, it left calcic formiate, which was identified by its characteristic behavior with argentic nitrate and mercuric chloride. The decomposition of mucophenoxybromic acid by potassic hydrate may therefore be expressed by the reaction:

$$C_4H_3(OC_6H_5)BrO_3 + H_2O = C_3H_3(OC_6H_5)BrO_3 + CH_2O_2.$$

While dibromacrylic acid passes readily into brompropiolic and malonic acids in an alkaline solution, phenoxybromacrylic acid is apparently unaltered by aqueous potassic hydrate. Even after

long boiling in a concentrated solution (2 : 1) no potassic bromide is formed.

Phenoxybrommaleic Acid.

On warming a solution of mucophenoxybromic acid with argentic oxide, metallic silver is readily formed. If the solution is then heated to boiling, and the silver precipitated by hydrochloric acid, the filtered solution deposits on cooling phenoxybrommaleic acid in the form of fine felted needles. Their melting point, when taken in the ordinary way, we found to be 103–104°; but when slowly heated, the melting point was materially lowered, probably through the formation of the anhydride. From the analysis of substance which had been dried over sulphuric acid, it would seem that here also a certain amount of the anhydride was formed, and that in this respect its behavior is perfectly analogous to that of dibrommaleic acid which is partially converted into anhydride by drying, as one of us has shown: [1]

I. 0.1213 gram of substance dried over H_2SO_4 gave on combustion 0.1935 gram CO_2 and 0.0245 gram H_2O.

II. 0.2204 gram of substance dried over H_2SO_4 gave 0.1494 gram AgBr.

	Calculated for $C_4H_3(OC_6H_5)BrO_4$.	Calculated for $C_4(O_2C_6H_5)BrO_3$.	Found. I.	Found. II.
C	41.81	44.61	43.51	
H	2.44	1.86	2.25	
Br	27.87	29.74		28.85

Ratio of carbon to bromine atoms as found = 10 : 0.995.

Argentic Phenoxybrommaleate. $Ag_3C_4(OC_6H_5)BrO_4$. By the addition of argentic nitrate to an aqueous solution of the acid, the silver salt is precipitated in the form of clustered rhombic plates, which may be recrystallised from boiling water without decomposition. The dry salt is decomposed suddenly by heat, but without detonation.

I. 0.3922 gram of the salt dried over H_2SO_4 gave on precipitation with HBr 0.2928 gram AgBr.

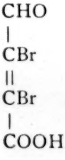
II. 0.2903 gram of the salt dried over H_2SO_4 gave on precipitation with HBr 0.2168 gram AgBr.

	Calculated for $Ag_3C_4(OC_6H_5)BrO_4$.	Found. I.	Found. II.
Ag	43.12	42.88	42.90

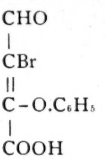
[1] This Journal **3**, 98; and Proceedings American Acad. of Arts and Sciences **16**, 178.

The relation which mucophenoxybromic acid bears to mucobromic is sufficiently shown by its conversion into phenoxybromacrylic and phenoxybrommaleic acids under conditions identical with those necessary to the formation of dibromacrylic and dibrommaleic acids from mucobromic. Furthermore, it is evident that the extreme stability of the phenoxybromacrylic acid in alkaline solution shows that the phenoxyl group has taken the place of the bromine atom which is so readlily removed from the corresponding dibromacrylic acid in the formation of brompropiolic acid.

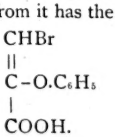
If mucobromic acid be written,



it follows that mucophenoxybromic acid has the form,



and the acrylic acid derived from it has the form,



REVIEWS AND REPORTS.

Report on Progress in Physiological Chemistry.

Liver, Bile, and Glycogen.

Facts acquired during the last few years concerning anatomical changes in the cells of the salivary, gastric and pancreatic glands in periods of *rest* and *activity*, and the connection of these changes with changes in chemical composition, have led several investigators to study the minute structure of the liver cells under like conditions, to trace, if possible, any connection here between structural differences and the secretion of bile or the formation of glycogen. Langley[1] has recently published a preliminary account of his results in the study of this question. The *resting* liver cells of the frog, toad, newt, pigeon and various mammals have certain common points of structure; the protoplasm is arranged in the form of a network, the meshes of which are nearly of the same size throughout the entire cell. Within the protoplasmic network is an interfibrillar substance, consisting of spherical granules, probably proteid in their nature, spherical globules of fat, and a hyaline substance filling up the spaces not occupied by the two former and consisting partly of glycogen and probably also of a proteid body. These spherical proteid granules described by Langley as present all through the resting cells have apparently been overlooked by previous investigators, even by Klein[2] and Kupffer. Apparently the best method for bringing out the granules and also the fat globules is to place a portion of liver in 1 per cent. osmic acid for 24 hours, then in alcohol for several days, after which sections can be cut. Sections thus prepared show the globules and granules imbedded in a homogeneous cell substance. Placed in iodine solution for a few minutes, portions of the interfibrillar substance of the cell take on a reddish-brown color, due to the presence of glycogen. The liver of a hungry frog, as in summer time, shows granules scattered equally throughout the cell with almost an entire absence of glycogen. During the long winter fast the cells undergo a decided change in appearance, the granules being more confined to the inner portion of the cell, forming a marked inner granular zone. At the same time the glycogen increases in amount, being stored up in the clear outer zone. The two zones are very clearly outlined in an osmic acid and iodine preparation.

[1] Proceedings of the Royal Society **34**, 20. [2] Quart. Journ. Med. Soc. n. s. **19**, 161.

As has been previously ascertained, the changes which take place during fasting in the cells of some of the gastric glands are very similar to the changes occurring during digestion. Likewise Langley has found in the liver of the frog that the changes which take place when the animal is fed are in nearly every respect like those which are gradually established during the winter fasting. The extent of the change, however, is dependent upon the state of the liver cells before the animal is fed, the change being much more marked when the cells start with a small outer non-granular zone. In such a case the outer zone becomes quite large by the 6th to 8th hour of digestion, while at the end of the 24th to 30th hour the cells become granular throughout. Langley observed that while a decrease of granules goes hand-in-hand with an increase of glycogen and an increase of granules with a decrease of glycogen, still a certain amount of variation may take place without any corresponding variation in the other, and thus Langley is led to the view that the formation of granules and the formation of glycogen are independent processes. But from analogy it seems fair to presume that the granules of the hepatic cells are destined to give rise to some one or more constituents of the bile, and Langley suggests that by proper chemical treatment these granules may be made to yield some portion of the bile salts.

In the study of the mammalian liver, Langley confined himself almost exclusively to the mole, with results similar to those mentioned in the case of the amphibian livers. In cells in which the digestive changes are less advanced, the glycogen may only partially surround the nucleus or may be accumulated more or less to one side of the nucleus. In no case did Langley observe the lumps or granules of glycogen observed by Kayser. Bock and Hofmann[1] experimented on rabbits, and found the glycogen accumulated in amorphous form around the nucleus. Langley's observations accord with theirs in this respect, although the former observer considers that the glycogen is stored up in the spaces of a protoplasmic network.

Quite independent of Langley, Afanassiew[2] has likewise studied the anatomical alterations of liver during different conditions of activity. Afanassiew's experiments were made mostly on dogs, the following general plan being adopted: First, the livers of animals deprived of food for a period of from one to three days were compared anatomically, with the livers of animals fed on a mixed or flesh diet, at the same time the amount of glycogen in the liver was determined in both cases. Very soon after the commencement of the experiment, a great difference was noticed in the structure of the liver, particularly in the cell elements and also in the quantity of glycogen, whereupon Afanassiew attempted to separate as far as possible the formation of bile from the formation of glycogen. For this purpose in the first series of experiments

[1] Virchow's Archives **56**, 201. [2] Pflüger's Archiv **30**, 385.

dogs were employed which had been fed purely on a carbohydrate diet, while in the other series the animals experimented on were fed on a purely flesh diet, meat or pure blood fibrin. The liver in each was examined quantitatively for glycogen. In still another series of experiments the secretion of bile was increased above the normal, without the use of food. This was accomplished by cutting the liver nerves of a curarized animal and then injecting pilocarpin into the blood, which materially increases the flow of bile.

Afanassiew noticed, conformable with the observations of Langley, that the liver cells of an animal fed on fibrin showed in general the characters of the liver cells of a hungry animal. As these cells are not colored brownish-red by iodine, and as the addition of osmic acid does not increase the granulations within the cell, Afanassiew concludes that by feeding with fibrin, the content of finely granular albuminous matter in the liver cell is increased. After feeding with potatoes and sugar, whereby the liver becomes exceedingly rich in glycogen, the liver cells appear very large, filled to excess with coarse granules or indistinct amorphous particles or spots of glycogen, with the protoplasmic network ordinarily not perceptible. The small sharply outlined granules which are so noticeable in the hungry condition, or after feeding flesh, are hardly ever to be seen. Again, if the formation of bile be increased by cutting the liver nerves, or by feeding with albuminoid food, the cells become correspondingly large, and contain between their protoplasmic threads, large numbers of fine, sharply outlined granules, which in chemical nature approach albuminoid matter. This fact explains the resistance of such cells to potassium hydroxide. When, on the other hand, the cells become relatively poor in albuminous matter, as during increased formation of glycogen, then the cells rapidly decompose in concentrated solutions of potassium hydroxide.

In a fat diet, fat globules are noticeable in the cell, and after taking mixed food, appearances due to a combination of all of the former are noticed. When a healthy animal is allowed to become hungry, the liver loses first the glycogen, then in part the water; the albumin remains the longest, although a portion of this is decomposed with formation of fat. There appears to be no division of cells with a difference in function, but all of the cells of the liver lobe form both bile and glycogen.

If an increased secretion of bile depends upon an increased circulation of blood, it would follow that a great accumulation of glycogen must diminish the secretion of bile, and Spiro[1] indeed found that the addition of carbohydrates to a flesh diet retarded the increase of bile secretion during digestion. As a result of experiments with toluylene-diamine Afanassiew found that the formation of bile is increased by an excessive decomposition of the red blood

[1] Du Bois Reymond. Archiv f. Physiol. Supplement Band, 1880.

corpuscles, from which it would appear that under normal circumstances the decomposition of the red blood corpuscles, within certain physiological limits, may give a stimulation to the secretion of bile.

Formation of bile coloring matter.—Tarchanoff[1] found, after injecting a solution of haemoglobin into the blood of a dog with a biliary fistula, a decided increase of coloring matter in the freshly secreted bile. This fact he considered as a support to the view of a conversion of the blood coloring matter into bilirubin outside of the liver. Stadelmann,[2] after calling attention to Tarchanoff's experiments, has given the results of his study of the question. The method employed in determining the coloring matter was based upon the use of the spectroscope according to the method of Vierordt.[3] In using this method, however, the bile must be examined as fresh as possible, since on standing exposed to air it acquires a green color, owing to the conversion of bilirubin into biliverdin by oxidation, and as the latter has far greater absorbing power, a higher percentage of coloring matter is obtained. Thus Stadelmann found that the coloring matter of a specimen of bile, after standing two days, increased from .074 per cent. to .110 per cent.

A large dog with a biliary fistula and fed upon a constant diet yielded in 12 hours, as a mean of 13 estimations, 147.5 cc. of bile with .082 gram of bilirubin = .0577 per cent. After injecting 20 grams of moist haemoglobin dissolved in 100 cc. of water into the jugular vein, a strongly bloody urine was passed, without however any icterus of the skin. Two hours after the injection a decided increase of the absolute quantity of bile coloring matter was noticed, while at the same time the quantity of bile was diminished. This was followed after 12 hours by an increase of the secretion of bile with a sinking of the relative content of the coloring matter. As compared with the normal average figure, the secretion of coloring matter in the first 12 hours showed an increase of .024, while in the second 12 hours an increase of .042 was noted. This would seem to indicate that the liver itself must first form bilirubin from the absorbed haemoglobin, and that Tarchanoff's view of the conversion of the haemoglobin into bilirubin in the blood itself is probably incorrect; for while bilirubin, as Vossius[4] has found, appears in the bile directly after its injection, and is secreted after 5 or 6 hours, an injection of haemoglobin solution does not produce an increased secretion of bile coloring matter until 3–4 hours after its injection, but on the other hand the secretion continues for 20–24 hours.

Stadelmann has likewise found that injection of .6–.8 per cent. sodium chloride solution produces in a similar manner a not inconsiderable increase of the absolute bilirubin secretion, there being

[1] Jahresbericht für Thierchemie **4**, 305. [2] Archiv f. exper. Pathol. u. Pharm. **15**, 237.
[3] Die Anwendung des Spectralapparates. Tübingen, 1873.
[4] Jahresbericht für Thierchemie **9**, 246.

at the same time a considerable diminution of the bile secretion. The bile itself becomes turbid and very noticeably green in color. This abnormal feature of the secretion Stadelmann considers due to an irritation of the hepatic cells or of the nerve endings in the liver caused by the abnormal condition of the blood.

Influence of food upon the composition of the bile.—It has usually been supposed that the composition of bile, or more strictly speaking the proportion of glycocholic to taurocholic acid, was a more or less constant one. Hüfner,[1] however, has found a decided variation in the amount of these acids contained in ox bile; thus, as a result of a large number of examinations, samples were obtained in which the two acids were present in approximately the same quantities, others in which the amount of glycocholic acid was fully five times larger than the amount of taurocholic acid. In the latter case the bile gave Hüfner's reaction with hydrochloric acid and ether quite easily; when, however, the taurocholic acid was in excess or even equal to the glycocholic acid, the crystallisation was not obtained. Emich[2] has found this non-crystallisation to be due apparently to the solvent action of the non-crystallisable taurocholic acid on the glycocholic. Hüfner has supposed this variation in composition due to the food. Carl v. Voit[3] has found, however, that this is not the case with dog's bile. Taking the determination of sulphur as an index of the amount of taurocholic acid, the following results were obtained:—

Animal.	Food Stuff.	Per cent. of Sulphur in dried Bile.	Per cent. of Sulphur in crystallised Bile.
Dog No. 3.	Flesh	2.24	4.52
" "	"	2.33	4.01
" "	Potatoes	1.90	4.25
" "	Gelatin	2.33	4.50
" "	Fat	3.14	4.61
" "	Potatoes	2.63	4.26
" " 4.	Flesh	2.68	4.47

According to Strecker and Hoppe-Seyler, dog's bile contains only taurocholic acid. These two investigators, likewise Bensch, as well as Bidder and Schmidt, found the amount of sulphur to correspond to about 6 per cent. Kunkel and Spiro, however, obtained results similar to the above.

By drawing away the bile, v. Voit finds that the amount of unoxidised sulphur in the urine is greatly diminished, which is in close agreement with the previously obtained results of Kunkel.[4] In normal animals the relation of unoxidised sulphur to sulphuric acid in a flesh diet is as 1 : 1.2, in a gelatin diet 1 : 5.5. In the case of a dog with a biliary fistula the relation in a flesh diet is 1 : 2.7, in a gelatin diet 1 : 6.2. Taurine is the main source of the unoxidised sulphur in the urine, though not the only one.

[1] Journal für prakt. Chemie **25**, 97.
[2] Monatshefte für Chemie **3**, 330.
[3] Jahresbericht für Thierchemie **12**, 417 et seq.
[4] Jahresbericht für Thierchemie **6**, 192.

According to all previous observers, the taking of food causes an increase in the secretion of bile. Hitherto, however, there has been a great divergence in the results obtained, due primarily to the lack of precision in arranging the diet and collecting the bile. As the amount of water in bile is exceedingly variable, the content of solid matter is the only certain indicator of the progress of the secretion. In hunger the secretion is not quite regular. The variations apparently depend on the irregular outflow of the then highly concentrated glairy bile. At night the secretion is diminished, due probably to the smaller decomposition of fat. After eating meat in large quantities, as for example 1266 grams meat and 398 grams of water, the maximum secretion takes place, 0.98 gram dry bile in the first hour, followed by a gradual sinking to 0.45 gram. The following table gives a few of the important results obtained by v. Voit, the figures giving the entire quantity of bile in grams secreted during the 24 hours, together with the amount of food taken.

DOG NO. 3.

Food.	Bile—Fresh.	Bile—Dry.
Hunger	124.3	8.46
"	78.8	7.26
750 flesh	272.4	12.16
1345 "	323.9	13.80
100 fat	173.7	7.43
1500 flesh and 130 fat	272.4	11.14
225 starch	132.0	8.81
545 bread	240.0	9.80
1764 potatoes	212.3	9.45
120 gelatin	150.5	7.37
150 "	202.7	10.76
1500 flesh and 76 gelatin	347.7	13.13

Thus in hunger only ½ to ⅓ of the usual quantity of bile is secreted. In the latter days of the hunger period, much less bile is secreted than in the first. Increased additions of albumin cause an increase of bile, though not a proportional one.

Bile perhaps originates only from the albumin, certainly it must in those cases where only albumin is decomposed. At the same time gelatin, carbohydrate and fat do not alter materially the quantity of bile, but as they spare the albumin they can thus indirectly aid the formation of bile.

Spiro considers the increase in the formation of bile after eating as due essentially to the decomposition in the liver of the absorbed organic matter. Voit, however, cannot accept this view, since the greatest increase of bile is noticeable during the first hour or so, at which time only a small portion of the food taken could be absorbed. It is more probably dependent on reflex action, or more probably still on the washing out of the thick, glairy bile of the hungry and night hours from the bile ducts and capillaries

by the water so abundantly absorbed. All observers have noticed the decided influence of water upon the secretion of bile.

Action of bile acids on proteid matter, etc.—It has long been an interesting question as to the probable action of the bile salts in the intestinal canal. Since the acids of the chyme are stronger than the bile acids, it follows that the latter will naturally be liberated by the former. The only thing in the bile itself which can act as a neutralising agent is a small quantity of acid sodium carbonate. When, however, the contents of the intestines react acid, free bile acids must be present. Lehmann long ago[1] recognised this fact, and various investigators[2] since then have demonstrated that the contents of the intestines, even to their entire length, ordinarily show an acid reaction, although the mucous membrane itself generally has an alkaline reaction. It is thus evident that in the intestines, as a rule, free bile acids are to be found, and not their neutral salts. Thus Maly and Emich,[3] in order to understand the behavior of the bile in the intestines, have made a special study of the behavior of the free bile acids towards the three albuminous bodies, egg-albumin, propeptone and peptone. The action of the pure bile acids on the above subtances has never been investigated, although Brücke, Schiff, Hammarsten and Moleschott have placed on record the results of their study of the so-called duodenal precipitate which is readily obtained when bile is added to the acid chyme or to an artificial pepsin digestion.

Maly finds that a one per cent. solution of taurocholic acid added to a one per cent. solution of peptone or propeptone produces an immediate white milky precipitate or turbidity difficult of filtration, which is easily soluble in dilute sodium carbonate, but reprecipitated by acetic or hydrochloric acid. The precipitate is very readily soluble also in solutions of soap, sodium glycocholate and taurocholate, even also in the slightly alkaline blood-serum. The precipitate formed as above is apparently not a compound of the peptone or propeptone with taurocholic acid, but a modified form of taurocholic acid itself. In fact, a solution of sodium chloride added to taurocholic acid produces the same effect as a solution of peptone. Peptone and propeptone appear to combine with taurocholic acid, but the compound is even more soluble than either of the two.

Cold saturated solutions of glycocholic acid are not precipitated by peptone solution. If, however, a solution of sodium glycocholate, peptone or propeptone and some hydrochloric acid are mixed together, a precipitate is obtained, which, however, contains but little if any peptone, mainly glycocholic acid.

Addition of taurocholic acid to a solution of egg-albumin produces an immediate, heavy flocculent precipitate, easily filtered,

[1] Lehrbuch d. physiolog. Chem. **2**, 69.
[2] Schmidt-Mulheim, Jahresbericht für Thierchemie **9**, 210. Uffelmann, *ibid.* **11**, 305. Nothnagel, *ibid.* **11**, 309.
[3] Monatshefte für Chemie **4**, 89, 1883.

which is readily soluble in all alkaline fluids, but is insoluble in alcohol, and contains both albumin and taurocholic acid. The latter however can be, in part at least, extracted by boiling with alcohol. Maly's experiments further show that the albumin is completely precipitated, more so even than when coagulated by heat, and that with proper precautions the method can be advantageously employed for quantitative purposes. Presence of large quantities of sodium chloride hinders the precipitation. Quantitative experiments also showed that taurocholic acid is an excellent agent for separating coagulable albumin from peptone or propeptone, the latter not being precipitated, while the former is completely so.

Glycocholic acid does not precipitate albumin. Thus these reactions, which may be assumed to take place in the intestinal canal, may serve to separate the coagulable albumin, rendering the peptones more readily absorbable, but whether the taurocholic acid precipitate is readily digestible is a question not yet answered.

Emich[1] has made a study of the antiseptic action of the bile acids and their behavior towards both the formed and unformed ferments. It has for a long time been considered that bile possesses antiseptic properties, although hitherto no experiments have been tried to verify this assumption. Emich has found that the presence of one per cent. of taurocholic acid in a solution or mixture will prevent the growth of bacteria in flesh and pancreas extracts, and that both lactic and alcoholic fermentation is hindered by its presence. Glycocholic acid in most cases acts in a similar manner, although not so energetically.

Brücke, Hammarsten and others have long ago demonstrated that the addition of a small quantity of bile to a pepsin digestion would completely suspend its activity. Emich has found that the presence of .2 per cent. taurocholic acid hinders the solvent action of gastric juice, while glycocholic acid is entirely without influence even when present to the extent of 1 per cent. In a similar manner the diastatic action of saliva and pancreatic juice is hindered by the presence of .2 per cent. taurocholic acid, and to a less extent by glycocholic acid.

R. H. CHITTENDEN.

(To be continued.)

THOMSEN'S "THERMOCHEMICAL RESEARCHES."

In the second volume of this work we find determinations of the most important combinations of the metalloids among themselves, including, therefore, many of the most valuable fundamental data of the science. A portion of this matter has appeared before, but is here revised and enlarged, while much is new, including the

[1] Monatshefte für Chemie **4**, 108, 1883.

study of the hydrocarbons and of carbontetrachloride and perchlorethylene, the latter amongst the most difficult thermochemical investigations yet accomplished. Perhaps as interesting a point as any that Thomsen has brought out relates to the formation heat of the hydrocarbons. In Vol. II he treats of only a few typical substances, viz. methane, ethane, ethylene, acetylene and benzene, the rest being reserved for Vol. IV; but he offers a formula for the calculation of the formation heat of hydrocarbons in general, knowing their structural formulae. The substance of this chapter appeared in the "Berichte der deutschen chemischen Gesellschaft," 13, pp. 1321-1324, and was reviewed in this Journal, vol. II, p. 347; but as the author in his second volume presents the subject in somewhat different form and with numbers revised, it will bear another brief review in this connection.

The method of calculation is based upon the following assumptions:

1. That heat is absorbed in the gasification of carbon, and that its amount is equal to the difference between the formation heat and combustion heat of carbon monoxide.

2. That the combination heat of the atoms of gaseous carbon with each other depends upon whether there is single, double or triple union.

3. That the combination of hydrogen and gaseous carbon is exothermic, and that all the hydrogen atoms of a molecule have the same influence upon its formation heat.

Now the formation of a hydrocarbon from amorphous carbon and hydrogen at 18° C., constant pressure, may be resolved into the following steps:

1. Gasification of amorphous carbon. Let the amount of heat required for this be represented by d for each atom.

2. Combination of carbon atoms with each other. Let the amount of heat evolved by this be represented by v_1, v_2, v_3, according as there is single, double or triple union.

3. The combination of hydrogen with the carbon nucleus. Let this combination heat be represented by r for each hydrogen atom.

4. Finally, the contraction to unit-volume (H_2); since the quantities are measured at constant pressure, an amount of heat q must be added for each volume (H_2) lost.

Hence, in general, the formation heat, H, at constant pressure, of a hydrocarbon, $C_nH_{v_m}$, equals

$$-nd + 2mr + \Sigma v + (m-1)q.$$

For the hydrocarbons in question, adopting the usual formulae and determining experimentally the combination heat, we have:

(1)	$CH_4 = -d + 4r + q$	$=$	21750 cal.
(2)	$C_2H_6 = -2d + 6r + v_1 + 2q$	$=$	28560
(3)	$C_2H_4 = -2d + 4r + v_2 + q$	$=-2710$	
(4)	$C_2H_2 = -2d + 2r + v_3$	$=-48170$	
(5)	$C_6H_6 = -6d + 6r + 9v_1 + 2q$	$=-1110$	

The formula for benzene used is based upon the supposition that there are nine single unions in the carbon nucleus.

As stated above, d equals the difference between the formation heat and combustion heat of CO, calculated for constant volume. This is given by Thomsen as 38380 cal.; also the value of q, calculated for 18° C., as 580 cal. From the equations 1, 2, 3, 4 and 5, the value of r, v_1, v_2, and v_3 may be calculated. These are given by the author as follows:

$$r = 14830,$$
$$v_1 = 15350,$$
$$v_2 = 14130,$$
$$v_3 = -1080.$$

He calls them the dynamic constants of carbon, and to them is added the combination heat of one atom of oxygen with the carbon nucleus, assumed to be the same as the combustion heat of CO, hence equal to 67670 cal. (constant volume).

The assumptions upon which this calculation is based seem somewhat hazardous; yet when the above values are used to calculate the formation heat in the five examples under consideration the accordance is extraordinary.

The following table shows the calculated results compared with the experimental.

	Formation Heat.		Combustion Heat.		
	Cal.	Exp.	Cal.	Exp.	
Methane	21520	21750	212160	211930	cal.
Ethane	28730	28560	370270	370440	
Ethylene	—2730	—2710	333370	333350	
Acetylene	—48180	—48170	310460	310450	
Benzene	—1990	—1110	788830	787950	

The calculated formation heat of benzene, assuming three single and three double unions, is —51700 cal., and combustion heat 838540. Thomsen carries the subject no further, except to refer to Vol. IV for the application of the formula and constants to a large number of compounds. If the result of so doing should justify the assumptions upon which the formula is based, it will be of the highest interest. Meanwhile there are some considerations which may well be borne in mind. In the first place these formation heats are determined only indirectly as the difference between the heat of combustion of the substance and of its constituent carbon and hydrogen in the elementary state. This difference is generally small compared with the combustion heat, and an error in the determination of the latter is increased many fold in the calculation of the formation heat. Take benzene for example; there is a difference of only 0.1 per cent. between the observed combustion heat and the value calculated from Thomsen's formula, whereas in the corresponding formation heat this difference becomes 79 per cent.

There is discrepancy too in the determinations of different observers. Thomsen himself, in the publication above referred to, gives for the formation heat of benzene —18960 cal., while Berthelot and Ogier give +5800; and for acetylene Berthelot gives —55100, for ethylene —9400 cal.

The following table shows the results obtained by applying Thomsen's formula to a few additional substances whose combustion heats have been determined experimentally:

	Cal.	Exp.
Propane, $CH_3—CH_2—CH_3$,	35940	30820 (Thom.)
Propylene, $CH_3—CH=CH_2$,	4480	760 (Thom.)
Allylene, $CH_3—C\equiv CH$,	—40971	—37500 (Berth.)
Dipropargyle, $CH\equiv C—CH_2—CH_2—C\equiv CH$,	—96250	—96390 (Thom.)
Diallyle, $CH_2=CH—CH_2—CH_2—CH=CH_2$,	—5350	+22700 (Berth.)
Aldehyde, C_2H_3OH,	+66450	+56500 (Berth.)

It would seem that in order to extend satisfactorily the application of his formula, Thomsen must be able to modify very considerably the constitutional formulae or the values for combustion heat already on record.

We find in an appendix to Vol. II a chapter on oxidising and reducing agents, and one on the constitution of certain substances, SiO_2 and HFl, in water solution. This latter, together with several chapters in Vol. III (which has appeared since this review was commenced), is of special interest, as affording instances of the application of thermochemical methods to the solution of important problems to which other methods hardly reach. We purpose to note briefly some of the author's conclusions in this direction. As to SiO_2 and HFl, the thermal phenomena seem to indicate that SiO_2 has no definite neutralisation point, at least for NaOH, water probably tending to decompose the silicate; that $Si(OH)_4$ is the correct molecular formula for the acid in water solution; that toward $Si(OH)_4$, HFl acts as a monobasic, diatomic acid of formula HFl_2H, the normal compound result from their action being $Si(Fl_2H)_4$.

As to HCl, the indication is that the true molecular formula for the acid in solution is HCl,H_2O or H_2ClOH, being monobasic. The author cites facts of isomorphism, molecular volume, and specific heat in further support of this view.

For iodic acid in solution the formula is $I_2O_4H_2$.

Continuing this line of investigation, we find a chapter in Vol. III on the dilution heat of certain acid, alkaline and saline solutions, published here for the first time. Sulphuric, nitric, phosphoric, acetic and formic acids are investigated, and no indication found of the existence in solution of definite secondary hydrates, not even of the crystallisable H_2SO_4,H_2O; the dilution heat being in general a continuous (hyperbolic) function of the amount of water used.

With regard to HCl, HBr, and HI there is found no indication of hydrate containing more than 2.2 or 2.8 molecules of H_2O to one molecule of acid, that being the composition of the most concen-

trated solution used; but there is evidence of the existence in concentrated solution of a hydrate containing one molecule of water; the formation heat of this hydrate is probably small, which accords with its instability. On the other hand, the author finds no evidence of a secondary hydrate in the case of the alkalies K, Na, NH_3, at least none containing more than three molecules of water.

Taking up next saline solutions, the author proposes two questions for investigation: first, whether dilution may cause a partial decomposition of the salt, and second, whether definite secondary saline hydrates exist in solution. With but 6 exceptions out of the 35 salts studied the following law is found to hold, viz. that those salts whose dilution heat is positive, dissolve when in anhydrous condition with evolution of heat; and those whose dilution heat is negative, dissolve with heat absorption. Now from his study of solution heats the author was led to conclude that those anhydrous salts and chlorine, bromine and iodine compounds which dissolve in water with heat evolution, form also crystallisable compounds with water (or are completely decomposed); and that those salts and chlorine, bromine and iodine compounds which form no crystallisable compounds with water (and are not fully decomposed) dissolve with heat absorption. And the author is therefore disposed to conclude that those substances which have a positive dilution heat form crytallisable combinations with water, while those whose dilution heat is negative form no crystallisable combination with water.

The next conclusion is that those salts which dissolve with heat evolution and crystallise with water also exist combined with water in solution; but that there is no indication of the existence of different saline hydrates in solution dependent on the quantity of water present; and that the dilution heat of acid, alkaline, and saline solution which is a function of the latter quantity is allied in cause to the heat disturbance which takes place on mixing liquids, such as alcohol with water, ether, chloroform, bisulphide of carbon, &c., which do not act chemically upon each other; and that the common cause is a transfer of energy between groups of different molecules, by which results an equilibrium which is not normal to the substance at the initial temperature, and hence produces an absorption or liberation of heat.

Upon these points Berthelot is not in accord with Thomsen. The former finds evidence in both the thermal and chemical phenomena of the existence of secondary hydrates, and makes them, as well as the partial decomposition of certain salts by water, play an important role in chemical statics.

Another chapter is upon a somewhat related subject, viz. the constitution of hydrated salts. In this are given the heats of combination of the anhydrous salt and its water of cystallisation, molecule by molecule; and the curious fact is brought out that in very many cases the latter taken in pairs have the same combination heat. The author suggests that this may be indicative of the symmetri-

cal relation of the water in the molecule of the hydrated salt, or, more probably, that the molecular weight of liquid water is double that of its vapor.

Another chapter is given to the determination of a large number of solution heats, and the remainder of the volume, with the exception of a special chapter on the energy and electro-motive force of galvanic combinations, is devoted to the principal combinations of the metals.

A. V. E. YOUNG.

NOTES.

On Trimethylene Derivatives.

By treating sodium ethyl aceto-acetate and other compounds of a similar character with bromine addition products of certain members of the unsaturated series of hydrocarbons, W. H. PERKIN, Jr., has succeeded in producing a number of interesting compounds which are derivatives of a body consisting of a closed chain of three or four carbon atoms.

The general method of formation involved in the production of these substances becomes evident by a consideration of the first one prepared, *i. e.* that obtained by the action of trimethylene bromide upon sodium ethyl aceto-acetate.

To a solution of sodium in absolute alcohol, ethyl aceto-acetate and trimethylene bromide were added in proper proportions, and the mixture heated for a time on the water bath. This resulted in the production of a substance to which the following formula was given:

$$\begin{array}{c} CH_2-CH_2-CH_2 \\ \diagdown\!\!\diagup \\ CH_3-CO-C-COOC_2H_5 \end{array}$$

The correctness of the empirical formula was proved by satisfactory analyses and by a vapor density determination. To this substance the name ethyl aceto-tetramethylene carbonate was given.

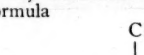
The acid corresponding to this ether was obtained by treatment with sodium ethylate and subsequent acidifying with sulphuric acid; it was obtained without difficulty in crystalline form. The formula was substantiated by analysis of the acid itself and of the silver salt. In order to be sure that this acid was the result of nothing more than simple saponification of the ether, the silver salt was treated with ethyl iodide, and, as indicated by the boiling point, the ether was thus reproduced.

The next transformation effected was the removal of carbon dioxide from the acid. This was accomplished by simple dry distillation by heating the acid on an oil bath to 180° C. Carbon dioxide was actively given off and a light volatile oil was distilled. The transformation thus effected is represented in the following equation:

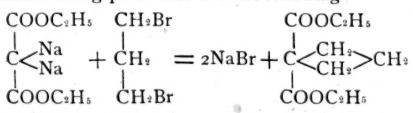
To this compound the name acetyl tetramethylene is given.

By treating sodium ethyl benzoyl-acetate with trimethylene bromide, by a process similar to the one already described in connection with the ether first considered, ethyl benzoyl-tetramethylene carbonate was produced. The formula of this substance is analogous to that of the corresponding acetyl compound, *i. e.*

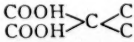
From this ether by saponification the acid was obtained, and from the latter by dry distillation the compound benzoyl-tetramethylene of the formula



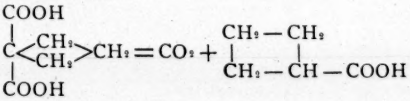
The compounds of special interest next produced are the mono- and dicarbonic acids of tetramethylene, which were obtained by starting with trimethylene bromide and sodium ethyl-malonate. The reaction taking place first was the following:



Saponification of this ether produced the dicarbonic acid of tetramethylene, *i. e.*

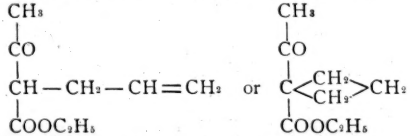


The monocarbonic acid was obtained from the dicarbonic acid by dry distillation thus:



Analyses of these acids, and of their salts, gave figures in accordance with the formula given.

Now let us consider the evidence upon which are based the structural formulæ of the compounds thus far considered, particularly with regard to the presence in them of this closed chain of carbon atoms known as the tetramethylene group. Referring in the first place to ethyl aceto-tetramethylene-carbonate, it is evident at first that one of two formulæ may be ascribed to it, either



The first corresponds to ethyl-allylaceto-acetate, the second contains a ring formed of four carbon atoms. The properties of the ether under consideration are, however, entirely different from those of ethyl allyl-aceto acetate, and therefore the second formula must be accepted as the correct one. The following general statements, applying to all the compounds discussed, are made:

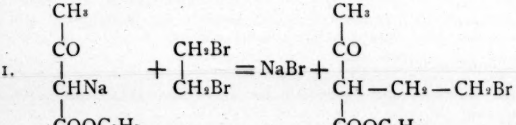
1. Comparing the allyl series with the tetramethylene series, the physical properties of isomeric members of the two series are found to be entirely different.

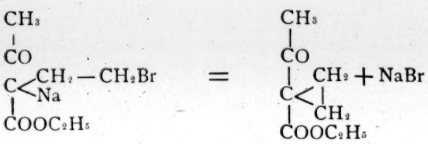
2. The compounds derived from ethyl-acetate and benzoyl-acetate show great stability in the operation of saponification with alkalies, while the isomeric allyl compounds are entirely broken up by similar treatment.

3. Finally, the allyl compounds furnish addition products with bromine, while the tetramethylene compounds produce only substitution products.

Although as yet tetramethylene has not been isolated, nor has an open chain of four carbon atoms been produced from the ring portion of any tetramethylene compound, the author hopes in future to be able to furnish desirable evidence of this character.

Compounds containing closed chains of three carbon atoms were obtained by operating with ethylene bromide upon ethyl aceto- and benzoyl-acetate. Thus in a similar manner to that already described, ethyl aceto-trimethylene-carbonate was produced; the action, as in the case of the analogous tetramethylene compound, taking place in two stages distinguished by successive treatments with sodium, thus:

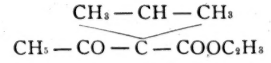


2. 

From this compound the acid and a number of salts were prepared. Analogous compounds from ethylene bromide and ethyl benzoyl-acetate were prepared, and in addition benzoyl-trimethylene, $C_6H_5-CO-CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$. Acetyl-trimethylene $CH_3-CO-CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$ was also prepared, but owing to lack of material was not identified until after the other trimethylene compounds had been described.

The action of hydroxyl-amine upon benzoyl-trimethylene resulted in the formation of benzoyl-trimethylene-oxime, having the following formula $C_6H_5-CNOH-CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$.

By treating sodium ethyl acetate with propylene bromide the compound ethyl acetyl-methyl-trimethylene carbonate of the formula



was produced. The formation of this compound shows that the kind of action which results in the formation of trimethylene compounds is of a *general* character, and not limited to one or two initial substances such as ethylene bromide.

The author hopes soon to publish additional papers bearing upon the oxime compounds, the formation of one of which has been mentioned.—(*Berichte der deutschen chemischen Gesellschaft* **16,** 208, 1787 and 2136; **17,** 1440.) W. C. D.

On Ferrous Chloride.

The experiments of Nilson and Pettersson in determining the vapor density of glucinum chloride, an account of which is to be found in the present number of this Journal, have led VICTOR MEYER to repeat the determination of the vapor density of ferrous chloride. Nilson and Pettersson having observed that the vapor of glucinum chloride is capable of corroding glass and porcelain,

Meyer remarks that it has become an important matter to reinvestigate, using platinum vessels only, those metallic chlorides, the determinations of whose vapor densities have been attended with difficulties. A redetermination of the vapor density of ferrous chloride seemed of particular interest, since heretofore it has been an undecided question whether to ascribe to this compound the formula $FeCl_2$ or Fe_2Cl_4. For his experiments Meyer used a pure, white specimen of the chloride, a determination of the chlorine in which gave the following figures:

	Found.	Calculated for $FeCl_2$.
Cl	55.68	55.90 per cent.

This was further purified by repeated sublimation in a stream of pure and dry hydrochloric acid gas.

It was found furthermore that, if this compound is heated in a difficultly fusible glass tube through which pure nitrogen is passed, most of the compound sublimes unchanged, but that a small quantity of a black residue is left behind, while in the sublimate a minute amount of the green crystals of ferric chloride can be detected. These circumstances were accounted for by assuming that the following reaction takes place:

$$3FeCl_2 = Fe_3Cl_6 + Fe.$$

The correctness of this assumption was supported by the fact that a replacement of the nitrogen atmosphere by one consisting of pure and dry hydrochloric acid gas resulted in effecting the sublimation of the entire quantity of ferrous chloride, leaving no residue and without the appearance of any abnormal body in the sublimate. The action of the hydrochloric acid in preventing the decomposition given above is assumed to be as follows:

$$Fe + 2HCl = FeCl_2 + H_2$$
$$Fe_3Cl_6 + H_2 = 2HCl + 2FeCl_2.$$

In view of the facts just considered, the determination of the vapor density was made in an atmosphere of hydrochloric acid; the vessel used was the porcelain tube previously recommended by the author.[1] In order to ascertain whether or not the use of the hydrochloric acid atmosphere was justifiable, a test determination of the vapor density of mercuric chloride was made, with a satisfactory result, *i. e.*

Found.	Calculated for $HgCl_2$.
9.55	9.36

In connection with ferrous chloride it was found that quite a high temperature is necessary for the volatilisation of this substance; at a red heat it takes place irregularly and very slowly, but at a yellow heat it becomes rapid and the results obtained agree fairly well.

[1] Berichte der deutschen chemischen Gesellschaft **12**, 1112.

The densities found are as follows:

I.	II.
6.67	6.38

The calculated values are for $FeCl_2$, 4.39; for Fe_2Cl_4, 8.78.

The value found is therefore the mean of the latter figures, and hence for ferrous chloride it seems that—as was proved conclusively by Züblin and Meyer for stannous chloride—this substance at lower temperatures consists of molecules of the formula Fe_2Cl_4, but that as the temperature rises these break up into molecules represented by the formula $FeCl_2$. The temperature reached in the above experiments was not, however, sufficiently high to produce entirely the latter molecular condition.

The author does not yet seem satisfied to leave the subject of the vapor density of ferrous chloride where it now stands, for although sure that when ferrous chloride is volatilised with use of glass and the hydrochloric acid atmosphere the glass is not at all attacked, he is not so confident in regard to the use of porcelain, and therefore expresses himself desirous of having opportunity to make the determination in platinum vessels.—(*Berichte der deutschen chemischen Gesellschaft* **17**, 1335.) W. C. D.

The Union of Bodies by Pressure.

Since the last report on this subject[1] W. SPRING has been experimenting with the view of showing that the heat produced by pressure is by no means as great as is generally supposed. In a late article[2] he states that the only difference between the views of Jannetaz and himself is in the explanation of the cause of combination. Jannetaz claims that the union of bodies by pressure is due to the heat evolved in the very act of compression, whereas he (Spring) claims that the only heat produced is caused by the rubbing of the particles against the walls of the enclosing vessel, and that in the apparatus used in his experiments this friction is reduced to a minimum. He then attempts to prove both theoretically[3] and experimentally that his view of the case is the correct one. A temperature of about 1000 degrees, he states, is necessary to fuse bell metal, so that if the shining coating, mentioned by Jannetaz as having been observed on a block of bell metal after compression, was due to the heat evolved by the pressure, the temperature arrived at must have been in the neighborhood of 1000°. Now in all his experiments the limit of contraction was reached before the piston had sunk in the cylinder one millimeter. Taking this as the distance through which the force acts, he shows that an equivalent of heat equal to .0165 calories is produced in effecting a pressure of 7000 atmospheres. This would produce in

[1] This Journal **6**, 129.
[2] *Ibid.* **17**, 1215.
[3] Berichte der deutschen chemischen Gesellschaft **17**, 1015.

his cylinder a temperature of only 40°.64, much below the fusing point of any of the substances used. In the calculation maxima are taken, and the above result could never be reached experimentally.

To verify the calculation, phoron, with a fusing point of 28°, was subjected to 7000 atmospheres pressure in a room whose temperature was 19°. Not the slightest indication of fusion was observable. Azoxy-benzene, fusing at 36°, was then tried with a similar result.

Another experiment was then undertaken to show that the friction between the particles of a mixture could not evolve any appreciable amount of heat. Ordinary gunpowder was subjected to 7000 atm. pressure. It formed a compact block, and in no case tried did it explode.

The melting of the bell metal is explained by the fact that Jannetaz compressed his filings between two plates, and that no attempt was made to prevent friction between these and the bell metal.

After showing that the union cannot be the result of fusion, Spring undertakes[1] to determine the amounts of the several compounds formed by successive compressions. He took copper, silver and lead, mixed them with sulphur in proportions to form CuS, Cu_2S, Ag_2S and PbS, and subjected the mixtures to pressure. The resulting block was then filed and a portion treated with carbon-bisulphide, and the amount of sulphide formed thus determined. The remaining portion was again subjected to pressure, filed and treated as before. The amounts of the sulphides formed after one, two, four and six compressions were found to be as follows:

	After one compression.	After two.	Four.	Six.
Ag_2S	4.51 per cent.	12.43 per cent.	46.74 per cent.	69.41
PbS	1.32	19.34	28.08	45.54
CuS	8.49	16.95	24.02	34.60
Cu_2S	14.09	28.20	40.08	56.89

The effect of filing was then investigated. A block of the pressed mixture containing 12.43 per cent. of silver sulphide was ground very fine and then examined, when it was found to contain 13.60 per cent.

Other blocks which had been prepared for some time were next examined, to determine the effect of duration of contact. A block composed of silver and sulphur which had been compressed and allowed to stand about a year, was found to contain 41.63 per cent. of sulphide instead of 12.43 per cent. A piece of copper and sulphur after four years contained 20.86 per cent. of cupric sulphide instead of 8.49 per cent.

As a result of the experiments it is shown that while pressure

[1] Berichte, etc, **17**, 1218.

exerts a strong influence in the union of bodies, the amount of the compound formed is dependent besides upon the duration of contact of the substances and the intimacy of the mixture, and cannot be accounted for upon the supposition of the evolution of great heat.

It is probable, therefore, that if Jannetaz had worked more carefully to prevent friction in his apparatus, and had subjected his substances to more than one compression, his results would have been more in accord with those of Spring.

W. S. B.

Gallisin, an Unfermentable Substance in Starch-sugar.

C. SCHMITT and A. COBLENZL have made a careful investigation of the unfermentable substances found in commercial starch sugars, and have succeeded in isolating a definite compound to which they give the name gallisin. The method of separation and purification which they made use of is as follows: 5 kilograms of commercial starch sugar were allowed to ferment. At a temperature of 18–20° C. and with a solution containing 20 per cent. the fermentation was complete in 5 to 6 days. It was filtered; the perfectly clear, almost colorless liquid evaporated as far as possible on the water-bath, and the syrup while still warm brought into a good-sized flask. The syrup was then well shaken with a large excess of absolute alcohol, when it became viscous, but did not mix with the alcohol. The latter was poured off, replaced by fresh alcohol and again shaken. When this shaking with alcohol has been repeated several times, the syrup is finally changed to a yellowish-gray mass. This is now brought into a large mortar, and rubbed up under a mixture of alcohol and ether. After some time the whole mass is transformed into a gray powder. It is quickly filtered off with the aid of an aspirator, washed with alcohol and then with ether, and brought under a desiccator with concentrated sulphuric acid. In order to purify the substance it is dissolved in water and treated with bone-black. The solution is then evaporated to a syrup, and this poured into a mixture of equal parts of anhydrous alcohol and ether. In this way the new compound is obtained as a very fine, pure white powder which rapidly settles. It has much the appearance of starch. Under the microscope it is perfectly amorphous. In the air it deliquesces much more rapidly than ignited calcium chloride.

Treated with dilute mineral acids or oxalic acid on the water-bath gallisin is transformed into dextrose. It does not ferment when treated in water solution with fresh yeast. The analyses lead to the formula $C_{12}H_{24}O_{10}$. When treated under pressure with three times its weight of acetic anhydride at 130–140° it dissolves perfectly. From the solution a product was separated which on analysis gave results agreeing with the formula $C_{12}H_{18}O_{10}$

$(C_3H_3O)_6$. The substance appears therefore to be hexacetylgallisin.

Physiological experiments on lower animals and human beings demonstrated clearly that gallisin has neither directly nor indirectly any injurious effect on the health.—(*Berichte der deutschen chemischen Gesellschaft*, **17**, 1000.)

The Atomic Weight of Glucinum.

A few years ago NILSON and PETTERSON concluded from their experiments on the specific heat of glucinum that the atomic weight of this element is 13.65, and not 9.1 as had generally been assumed. Lothar Meyer attempted to show that their results are capable of a different interpretation, quite in harmony with the atomic weight 9.1. Afterward Nilson replied to Meyer, and, taking into account the specific heats of the oxide and sulphate of glucinum, found confirmation of his view that the atomic weight is 13.65. If this figure is correct, the periodic law receives a serious blow, as with the larger atomic weight, glucinum cannot be fitted into the scheme which is based on the law. Nilson and Petterson have recently determined with great care the specific gravity of glucinum chloride in gas form, and find that it corresponds to the formula $GlCl_2$ in which the atomic weight of the metal is 9.1. They conclude their interesting paper with these words: "In view of these results and the fact that Avogadro's law is without exception in the whole field of chemistry the basis for the conception of the molecule, we must give up the idea formerly held by us that glucinum is a trivalent element, which we were led to by the agreement of the atomic heat ($Gl''=13.65$) with the law of Dulong, and the numerous analogies between the physical constants (molecular heat and volume) of the compounds of glucinum on the one hand and of the rare metals scandium, erbium, yttrium, &c., on the other. While recognising in this important case the validity of the periodic law, we at the same time call special attention to the peculiar fact that the laws of Dulong and Avogadro lead to exactly opposite conclusions regarding the atomic weight and valence of the element glucinum, a fact which is unparalleled in the field of metallic elements." —(*Berichte der deutschen chemischen Gesellschaft*, **17**, 987.)

Dumas and Würtz.

It is not too late to record the great loss which chemistry has suffered recently in the death of the two leading French chemists, JEAN BAPTISTE ANDRE DUMAS and ADOLF WÜRTZ.

Dumas had reached a good old age, his best work having been done many years ago. His most important investigations were on the *relations of the molecular volumes of aeriform substances;*

and *on types*, in which he showed that the properties of chemical compounds depend not only upon the nature of the elements of which they are composed, but also upon the manner in which these elements are arranged, upon the *type* to which the compound belongs. This investigation on types was very fruitful, and, though Dumas' conception of types was indefinite, and to a considerable extent artificial, our present views regarding the constitution of chemical compounds are based largely upon this conception.

Dumas also did a great deal towards the accurate determination of atomic weights.

Würtz was a much younger man than Dumas, though he was born in 1817. He had long been a leader in the chemical world. Some of his investigations were of fundamental importance, particularly that on the *substituted ammonias*, the preparation of which gave definiteness to the conception of types due to Dumas, and thus led to the idea of valence; and that in the *diatomic alcohols*, in which he discovered glycol, and, comparing this with ordinary alcohol and glycerin, was led to the recognition of the polyatomic radicals, which in turn led to the recognition of the valence of the elements.

Both Würtz and Dumas were voluminous writers. In 1828 Dumas published his "Traité de chimie appliquée aux arts" in eight volumes. Among the many volumes written or edited by Würtz may be mentioned the "Dictionnaire de chimie pure et appliquée," "Theorie atomique," and "Leçons élémentaire de chimie moderne."

A new and valuable feature will be introduced this year in the meetings of the Chemical Section of the American Association for the Advancement of Science. Prof. J. W. Langley, the presiding officer of the section, has selected two topics for discussion, which have been approved by a majority of the members. The topics are:

1. To what extent is the hypothesis of "Valence" or "Atomicity" of value in explaining chemical reactions?
2. What is the best initiatory course of work for students entering upon laboratory practice? What are the best methods of illustrating chemical lectures?

If the meeting is well attended, and the discussions properly introduced, good results will be sure to follow.